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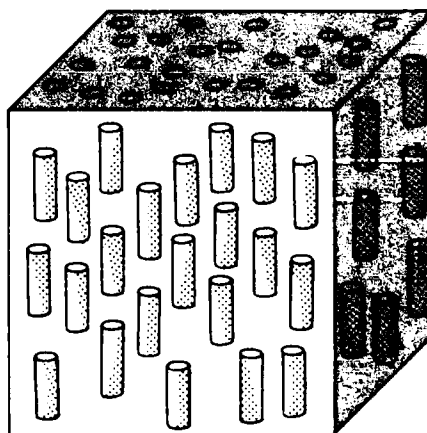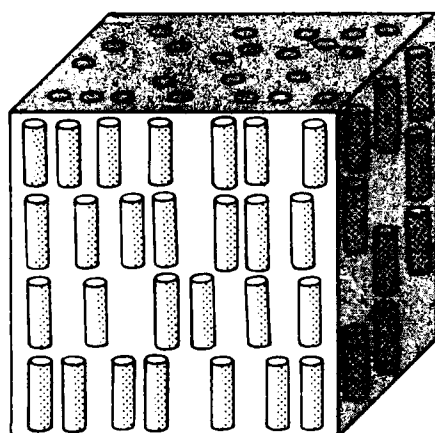
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The remarkable mechanical properties and thermal stability of fibers fabricated from liquid crystalline polymers (LCPs) have led to the use of these materials in structural applications where weight savings are critical. Advances in processing of LCPs could permit the incorporation of these polymers into other than uniaxial designs and extend their utility into new areas such as nonlinear optical devices. However, the unique feature of LCPs--intrinsic orientational order--is itself problematic, and current understanding of processing with control of orientation falls short of allowing manipulation of macroscopic orientation (except for the case of uniaxial fibers). This report reviews the current and desirable characteristics of LCPs and identifies specific problems and issues that must be addressed so that advances in the use of these unique polymers can be expedited.

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Liquid Crystalline Polymers

Report of the
Committee on Liquid Crystalline Polymers

NATIONAL MATERIALS ADVISORY BOARD
Commission on Engineering and Technical Systems
National Research Council

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Cover: Schematic arrangement of molecules in the smectic phase (top left) and the nematic phase (bottom right) of a liquid crystalline material.

ABSTRACT

The remarkable mechanical properties and thermal stability of fibers fabricated from liquid crystalline polymers (LCPs) have led to the use of these materials in structural applications where weight savings are critical. Advances in processing of LCPs could permit the incorporation of these polymers into other than uniaxial designs and extend their utility into new areas such as nonlinear optical devices. However, the unique feature of LCPs—intrinsic orientational order—is itself problematic, and current understanding of processing with control of orientation falls short of allowing manipulation of macroscopic orientation (except for the case of uniaxial fibers). This report reviews the current and desirable characteristics of LCPs and identifies specific problems and issues that must be addressed so that advances in the use of these unique polymers can be expedited.

PREFACE

The subject of liquid crystalline polymers (LCPs) transcends classical polymer chemistry and physics, and it extends the conventional boundaries of rheology and processing. Properties of these new materials are, on the one hand, reminiscent of amorphous metals, while simultaneously exhibiting attributes of organic single crystals. In this report we attempt to evaluate the potential of LCPs in selected areas, pointing out obstacles to further progress and suggesting where efforts in research and development might expedite LCP utilization in current and new technologies.

Because the subject touches on a wide range of topics, we have attempted to make this report accessible by adhering to a parallel presentation scheme. Thus, insofar as possible, the key chapters of the report are divided into the following headings:

Macromolecular Design and Synthesis
Understanding and Theory
Processing
Mechanical Properties
Blends and Composites
Nonlinear Optical Properties

When useful, the headings are subdivided further into sections on lyotropic (solution processed) and thermotropic (melt processed) LCPs. Occasionally, one of these sections may be partitioned into separate subsections, e.g., mainchain and sidechain LCPs. We have also tabulated a glossary of abbreviations and acronyms (Appendix B).

The report is intended to enable persons unfamiliar with the field to obtain a general appreciation of LCPs in the context of conventional polymers (see Chapter 2, Background) and to proceed to contemporary issues associated with specific topics (e.g., nonlinear optical characteristics of LCPs). We include an appendix indicating approximate current federal funding levels for research on these new classes of polymers (Appendix A).

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EXECUTIVE SUMMARY

The unique feature of liquid crystalline polymers (LCPs)—high local (microscopic) orientational order, which is retained in the solid state—has significant implications in a range of DOD applications utilizing polymers. The remarkable mechanical properties and thermal stability of fibers from precursor liquid crystalline solutions (lyotropic spinning dopes) are the principal driving forces that launched these materials and encouraged efforts to place LCPs in structural applications where weight savings are critical.

It would appear that advances in processing the lyotropic polymers could allow the incorporation of LCPs into other than uniaxial designs—multiaxially oriented items. Moreover, novel processing might make thermotropic LCPs eligible for critical structural applications. However, the unique feature of LCPs is itself problematic—the current understanding of processing with control of orientation falls short of permitting deliberate manipulation of macroscopic orientation (with the exception of uniaxial fibers). Even carefully designed applications that exploit other features of liquid crystallinity (anisotropic thermal expansivity, transport anisotropy, optical characteristics, etc.) will be retarded until there is an in-depth understanding of how processing promotes morphology in conjunction with how molecular structure affects the mechanical and the unusual physical properties of these new classes of polymers.

The principal conclusions of the committee are as follows:

• New cost-effective synthetic efforts and stabilization techniques are required to manipulate and maintain sequence distribution and thereby control polymer properties.

• Theories of LCP behavior must address polymer flexibility to realistically predict blending, rheological, and chain dynamical properties of ordered polymer phases.

• Processing protocols must go beyond conventional methodologies, e.g., explore solid-state forming of LCPs in efforts to achieve multiaxial order and obviate macroscopic heterogeneity.

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- Compressive failure mechanisms must be understood in order to suggest solutions to current mechanical limitations of LCP applications; simultaneously, new nonstructural applications of LCPs (e.g., as barrier materials) should be explored.

- LCPs may find extensive applicability in blends and composites. However, the roles of LCPs as the dispersed phase or as the matrix phase, filler shape and adhesion (and self-adhesion) are complex and poorly understood issues.

- Lowering the cost of LCP in products through lower cost monomer, polymerization and fabrication processes will catalyze the overall acceptance and range of applications of LCPs by the user community.

- An interdisciplinary effort is required to exploit the anisotropy of LCPs in nonlinear optical applications.

- The current annual Federal funding level for LCP research is almost $10 million.

- LCPs and their unique advantages as structural polymers were discovered and developed in U.S. industrial research laboratories in the 1960s and 1970s. A cursory glance at the following table suggests that current research and manufacturing effort has now become worldwide.

Companies Engaged in LCP Development		
United States	Western Europe	Japan
Allied-Signal	Akzo	Asahi
Amoco (Dartco)	BASF	Denki Kagaku
DuPont	Bayer	Idemitsu
Eastman	DSM	Kuraray
Hoechst Celanese	Hoechst	Mitsubishi Chemical
Monsanto[1]	ICI	Mitsubishi Gas
	Montedison	Mitsui Toatsu
	Rhône-Poulenc	Nippon Petrochemical
		Polyplastics
		Sumitomo
		Teijin
		Toray
		Toyobo
		Unitika

[1]Has stopped research

Source: Outlook for Advanced Engineering Materials: Plastics, Composites and Ceramics. November 1986, R861101. Cambridge, Mass.: Arthur D. Little Decision Resources.

Committee discussions frequently returned to economic and geopolitical topics, about which it was collectively agreed that members were ill-equipped to make meaningful recommendations. Nevertheless, two of these issues deserve attention:

• There was a consensus that meaningful evaluation of new (and potential) LCP systems is severely hampered by a limited number of facilities in the United States wherein intermediate-scale monomer and polymer synthesis [between the lab-bench scale (~100 g) and pilot plant (100 to 1000 lb)] can be carried out.

• Although many companies are market developing LCPs, large volume use awaits lower cost polymers.

Therefore, LCPs are a fertile area warranting intensive study. The findings will have an impact on a wide range of problems that include mechanical and optical properties of polymers. Moreover, it is anticipated that the findings on LCPs will lead to a more comprehensive understanding of conventional polymers and their fabrication techniques.

1

CONCLUSIONS AND RECOMMENDATIONS

The following are the major conclusions and recommendations. More detailed information can be found in the following chapters of the report.

MACROMOLECULAR DESIGN AND SYNTHESIS

Thermotropic LCPs (Mainchain)

Conclusions

• Among the serious molecular design issues affecting copolyester syntheses are the elucidation and control of the mer sequence along the polymer backbone. Until these are accomplished, the structure-property relationships associated with backbone sequence will be unclear and subsequent design of improved polymers will be severely hampered. Future challenges facing widespread utilization of thermotropic LCPs are economic in nature. It is necessary to develop higher-temperature properties utilizing lower-cost monomers, i.e., to develop low-cost syntheses of key (naphthalene- and biphenyl-based) monomers or to develop new low-cost (aromatic) monomers.

Recommendations

• Develop new polyester polymerization techniques with the associated catalysts and transesterification inhibitors that yield and maintain specific mer sequences.

• Continue efforts to measure mer sequence distribution, e.g., by multinuclei NMR.

• Develop high-temperature properties utilizing lower-cost aromatic monomers, e.g., hydroquinone.

• Develop efficient direct coupling of simple monoaromatic functional molecules to prepare low-cost biphenyl A-A and A-B monomers, e.g., A = -COOH, B = -OH.

Thermotropic LCPs (Sidechain)

Conclusion

• Sidechain LCPs have great potential as functional polymers. Development of properties dependent on noncentrosymmetric structures such as certain nonlinear optical effects, piezoelectricity, and pyroelectricity is possible via selective chemistry. Ferroelectric behavior has been observed in smectic C sidechain LCPs. Since surface-stabilized ferroelectric liquid crystals are in a sense "self-poling," a combination of ferroelectric and, for example, nonlinear optical properties in a single material would be attractive. In addition, sidechain LCPs as elastomers and as high-performance coatings warrant more consideration.

Recommendations

• Create opportunities that exploit novel functional sidechain LCPs via the interplay of function and chemical structure in these anisotropic systems, particularly in areas where their structural anisotropy and elastomeric and/or glassy mesophase formation can lead to new applications and enhanced performance, e.g., optical storage and waveguide media.

• Encourage design and synthesis of sidechain LCPs for nonlinear optical properties in integrated programs of characterization and evaluation.

• Develop synthesis of sidechain LCPs that exhibit novel properties such as ferroelectricity, ferromagnetism, and elasticity.

• Evaluate sidechain LCPs as coatings on substrates and as films for use as potential high-performance materials.

Lyotropics

Conclusion

• Perhaps the biggest challenge in the future of advanced high-performance materials from lyotropic polymers will be the development of low-cost synthetic routes to these more complex polymer precursors, and subsequent facile polymerization schemes. Both factors are essential for a consistent and ample supply of polymer from commercial sources. Reliable and reproducible supply is, in turn, a prerequisite for evaluating processing procedures that are directed toward fabricating bulk sample alternatives to uniaxial materials.

Recommendations

• Seek compositional modifications of aramid and benzobisoxazole (thiazole) polymers that enhance solubility in innocuous solvents while maintaining properties of the polymers in the solid state.

- Pursue compositional concepts that lower rigid monomer costs and/or facilitate polymerization of rigid rod polymers.

THEORETICAL UNDERSTANDING

Single Polymer Systems

Conclusion

- Rigid-rod theories have been extended to include the influence of macromolecular flexibility on the order parameter and phase transitions in both lyotropic and thermotropic systems.

Recommendations

- Test predictions with unequivocal data from polymer systems that conform to the theoretical assumptions.

- Extend the theories to deal with other, perhaps dominant features of LCPs, such as polydispersity, the onset of gelation/aggregation, and macroscopic heterogeneities.

Blends

Conclusion

- Blends of LCPs with LCPs and of LCPs with flexible polymers are of potential importance. An adequate theoretical framework of blends to guide experimental work is lacking. For example, the extent to which miscibility would be enhanced or decreased because of differences in rigidity in the component chains is not understood.

Recommendation

- Perform further theoretical and experimental investigations of phase equilibria of LCP-containing blends.

Dynamics

Conclusion

- Chain dynamics dominate both phase transitions and the development of structure during processing. Although there has been progress on the theory of diffusion and rheology of rigid-rod polymers in dilute and semidilute solutions, very little is known about these properties in liquid crystalline solutions and bulk polymers. This lack of understanding of chain dynamics has an impact on processing and property issues, such as adhesion, phase decomposition and nucleation, and orientation development in complex molded parts.

Recommendations

- Investigate intensively the dynamic behavior of the anisotropic phase.

- Encourage theoretical studies of the rheology of LCPs.

PROCESSING

Lyotropics

Conclusion

- The technology for the formation of highly oriented fibers from anisotropic polymers is well established, but fabrication processes for biaxially oriented films and other multiaxially oriented shapes are still under development. Process development appears to be feasible with existing commercial lyotropic LCPs (e.g., Kevlar®); these processes should carry over to new polymers with little modification.

Recommendation

- Continue process development (with better and more volatile solvents) for high-performance multiaxially oriented shape formation using commercially available LCPs, including post forming and/or other modifications for specific applications.

Thermotropics

Conclusion

- Melt spinning of highly oriented fibers is under commercial development by a number of companies. However, such efforts in injection molding face problems because of the tendency to form highly oriented local regions. This in turn leads to poor uniformity of macroscopic properties and weak weld lines. The current meager understanding of melt flow precludes systematic advances in mold design to overcome these problems. Solid-state processing is one area offering promise for overcoming the problems associated with flow-induced anisotropy.

Recommendations

- Increase effort to understand the flow of LCPs; place emphasis on efforts to overcome macroscopic heterogeneity and on studies that yield sufficient background to design molds with mechanical solutions to the weld line problem.

- Encourage research on solid-phase processing.

- Fund on a case-by-case basis specific fabrication processes to exploit unique properties, e.g., poling in electro-optical applications.

MECHANICAL PROPERTIES

Conclusions

• The general consensus is that poor compressive strength of uniaxial LCP materials is a major limitation in their utilization in structural materials. The situation is exacerbated by a poor understanding of how the anisotropic strength (longitudinal covalent and lateral dispersion and/or hydrogen bonding) manifests itself throughout the morphological hierarchy in the solid state—macromolecule to bundling of fibrils. Efforts to fabricate stronger materials via cross-linking are inconclusive. As with conventional composites, adhesion of LCP fibers to the matrix is problematic.

• The influence of temperature on mechanical properties is more important in melt-processible LCPs than in the case of the thermally stable lyotropic LCPs.

• Since self-adhesion in LCPs is poor, the weld line problem in injection-molded parts is exaggerated and may be insurmountable at the molecular level. This also manifests itself as a tendency for fibrillation in uniaxial films and limits their usefulness; efforts to superimpose biaxial order on films are being pursued. Advances could be expedited by pursuing film processing studies on readily available LCPs.

• Environmental exposure, whether natural or application-imposed, can lead to deterioration of LCP-based structures and articles. This concern is not fatal because adequate protection can be provided if the need is recognized. For military materiel, the chemical warfare (CW) scenario is considered to be part of the application-imposed environment and, although some LCPs exhibit excellent barrier properties, exposure to CW liquids must be included in any screening protocol during materials selection and qualification.

Recommendations (in addition to recommendations cited under **Processing** *et al.)*

• Encourage research directed toward identifying the compressive failure mechanism in LCPs, in particular delineating the level (microscopic versus macroscopic) at which the failure is initiated.

• Screen LCP materials to establish resistance to natural and end-use environments that include exposure to CW liquids.

• Encourage the evaluation of diffusion and permeability in LCPs that may be utilized as barrier materials.

BLENDS AND COMPOSITES

Conclusion

• The combination of LCPs with other materials to control the balance of properties and improve cost-effectiveness is clearly an important technology area for increasing the overall utility of LCPs. The problems inhibiting the rapid development of this technology are the same as those slowing LCP acceptance in other areas. These include high property anisotropy in finished parts, poor compressive strength, and poor adhesion to conventional and mesogenic materials. This is not in contradiction to the observations that fillers and blending can mitigate many of these effects but, is rather an important hint into what the underlying controlling parameters of the science must be. Hence, from both the scientific and technological points of view, investigations of the behavior of LCPs in multicomponent systems should be strongly supported.

Recommendations

• Investigate the effect of shape, surface chemistry and properties of filler particles, as well as processing methods, on the orientation and properties of the LCP phase.

• Understand and improve LCP adhesion to fillers, to conventional polymers, and to other LCPs.

• Understand the dynamics and equilibrium of phase shapes, sizes, and properties of multicomponent systems that include LCPs.

NONLINEAR OPTICAL PROPERTIES

Conclusion

• Liquid crystallinity in combination with the unique electronic properties that can be achieved in organic molecular solids and polymers may lead to useful polymeric materials for second- and third-order nonlinear optical applications. The advantageous property associated with liquid crystallinity is anisotropic order, which is either essential to or enhances nonlinear coefficients and imparts stability to the critical orientation of chromophores in the films. The complex issues associated with the range of properties that must be achieved will require substantial interdisciplinary efforts.

Recommendations

• Support initiatives aimed at understanding and achieving <u>stable</u>, uniform polar alignment in polymeric materials for second-order nonlinear optical applications.

• Support polymeric design, synthesis, and processing studies aimed at the unique properties of waveguide structures for third-order nonlinear optics.

• Focus research support in polymer nonlinear optics on interdisciplinary programs where molecular and polymer design and synthesis, waveguide design and fabrication, and physical characterization are combined.

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BACKGROUND

Relatively unhindered rotation about the single bonds in the backbone of most macromolecules means that a random trajectory for the polymer chain is the most common polymer conformation. Features of some special monomers (resonance, stereochemistry, etc.), however, restrict internal degrees of freedom in the polymers such that the mainchain is extended in space along an almost linear trajectory. Extended polymer chains or chain segments can, through excluded volume interactions, lead to long-range orientational ordering of the macromolecules—liquid crystallinity—in concentrated solution or in the melt. Liquid crystals (LCs), sometimes also called mesophases, were first recognized in low-molar-mass compounds a century ago, and they enjoy widespread technological applications because of their unique electro-optical properties. Low-molar-mass LCs are highly anisotropic fluids that exist between the boundaries of the solid state and the conventional isotropic liquid state and exhibit features of both states. In the case of macromolecules, orientational ordering of extended polymer chains is sufficient to impart some crystal-like orientational ordering to their fluid phases—melts or polymer solutions. Although this orientation is very subtle on a local scale (it is masked by the rapid and complex molecular dynamics characteristic of all fluid phases), time-averaged attributes of these fluids are anisotropic and therefore dramatically different from those same attributes in ordinary isotropic liquids. Figure 2.1 exaggerates the differences between the melt of a conventional random coil polymer (top) and that of a liquid crystalline polymer (LCP) (bottom) in order to pictorially show the long range order in a fluid phase of the LCP. In LCP melts or solutions this average anisotropy has dramatic consequences. When macroscopic uniform alignment of local directors exists, such fluids exhibit bulk anisotropic dielectric, magnetic, optical, transport, etc., properties. Materials formed from polymers that are orientationally organized in the fluid state retain this anisotropy in the solid state and frequently exhibit ultrahigh strength and stiffness (modulus) along the machine direction (parallel to the extended chains) because the organization and conformational preferences of the chain promote an extended-chain crystal habit. For these

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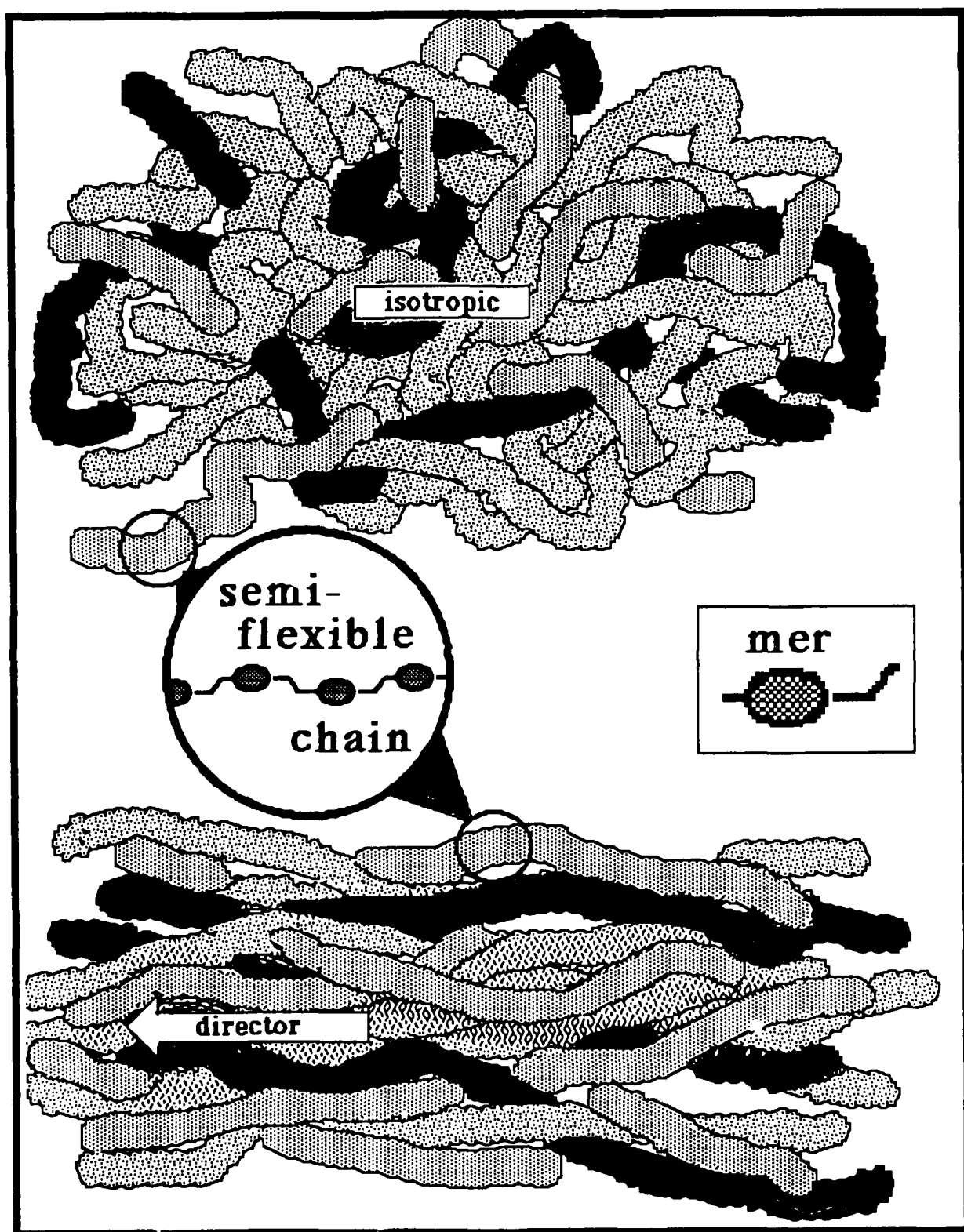
FIGURE 2.1 Schematic indication of the differences between an isotropic (top) and a liquid crystalline (bottom) polymer fluid.

reasons, LCPs are being increasingly utilized in specialty and high-performance applications. Historical reviews (Economy, 1989; Jackson, 1989; Samulski, 1985; and Dobb and McIntyre, 1984), general introductions (Browstow, 1988; Chapoy, 1985; Finkelmann, 1987; and Samulski, 1982), and contemporary reviews of LCP properties (Calundann et al., 1988; and G. E. Williams, 1987) abound.

LCs and LCPs may be divided into two broad categories, according to the principal means of achieving fluidity. Lyotropic LCPs result from the action of a solvent and hence are multicomponent polymer solutions—polymer plus solvent(s). Thermotropic LCPs are produced by heat and may be single (neat polymer) or multicomponent melts.

Within each category, three distinctive supramolecular organizational or structural classes of LCs have been identified: the nematic, smectic, and twisted nematic or cholesteric phases. Structural differentiation of these phases is related to the packing aspect and dimensionality of the translational organization of the molecules. In the examples of these phases we limit consideration to mainchain LCPs. Nematic LCs are distinguished by a unique director (optic axis) in the fluid; the nematic director is established by the parallelism of the long axes of molecules ([average] polymer chain axes). There is no translational order in this nominally uniaxial fluid (Figure 2.2).

Chain parallelism also characterizes the smectic phase, but translational order is also present in the form of long-range stratification normal to the chain axes (Figure 2.3). Mobility of the entire chain within the smectic layers is possible, although this increased translational organization lowers chain mobility relative to nematic phases. (In low-molar-mass LCs bulk fluidity in the smectic structure involves the layers gliding past one another; such a transport mechanism would be sharply attenuated in polymeric analogs, wherein a single semiflexible chain traverses more than one layer; smectics formed from rigid rod polymers with the layer spacing equal to the rod length might exist.) (Wen et al., 1989) In nematic phases chain ends (defects) are randomly distributed in the ordered fluid; there may be a tendency for such defects to segregate between layers in smectic fluids composed of semiflexible chains. Cholesteric LCs are similar to nematics in organization, with the additional feature of a cumulative twist between molecules, a result of the asymmetry of intermolecular forces. This asymmetry is due to the presence of chiral centers in these mesogens. As a result, the local nematic director twists into an inherently biaxial, helicoidal supramolecular structure (Figure 2.4). Although there is a large number of applications of cholesterics in low-molar-mass LCs that exploit their optical properties (temperature sensors, notch filters, etc.), there is little evidence of widespread use of this biaxial superstructure in LCPs.
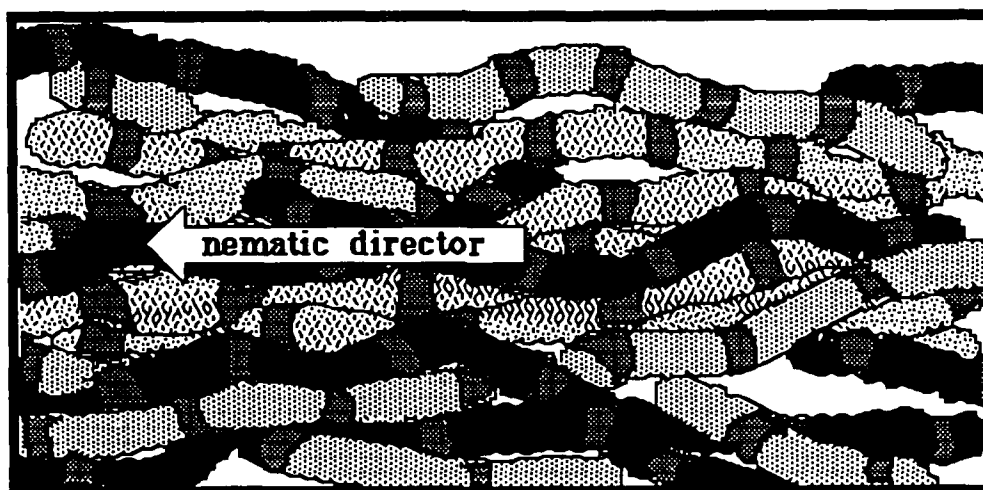
FIGURE 2.2 An absence of translational order in the idealized nematic.
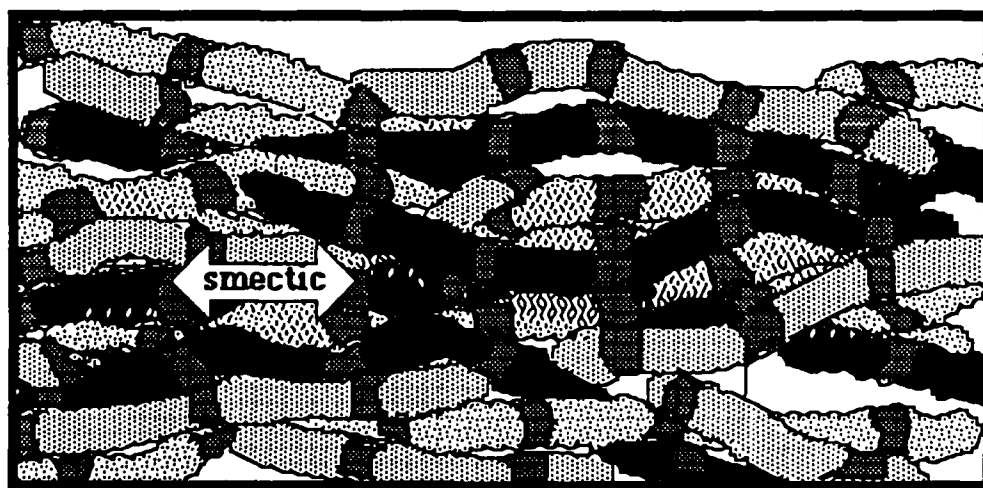
FIGURE 2.3 Smectic stratification (lateral registration) in a polymer mesophase.

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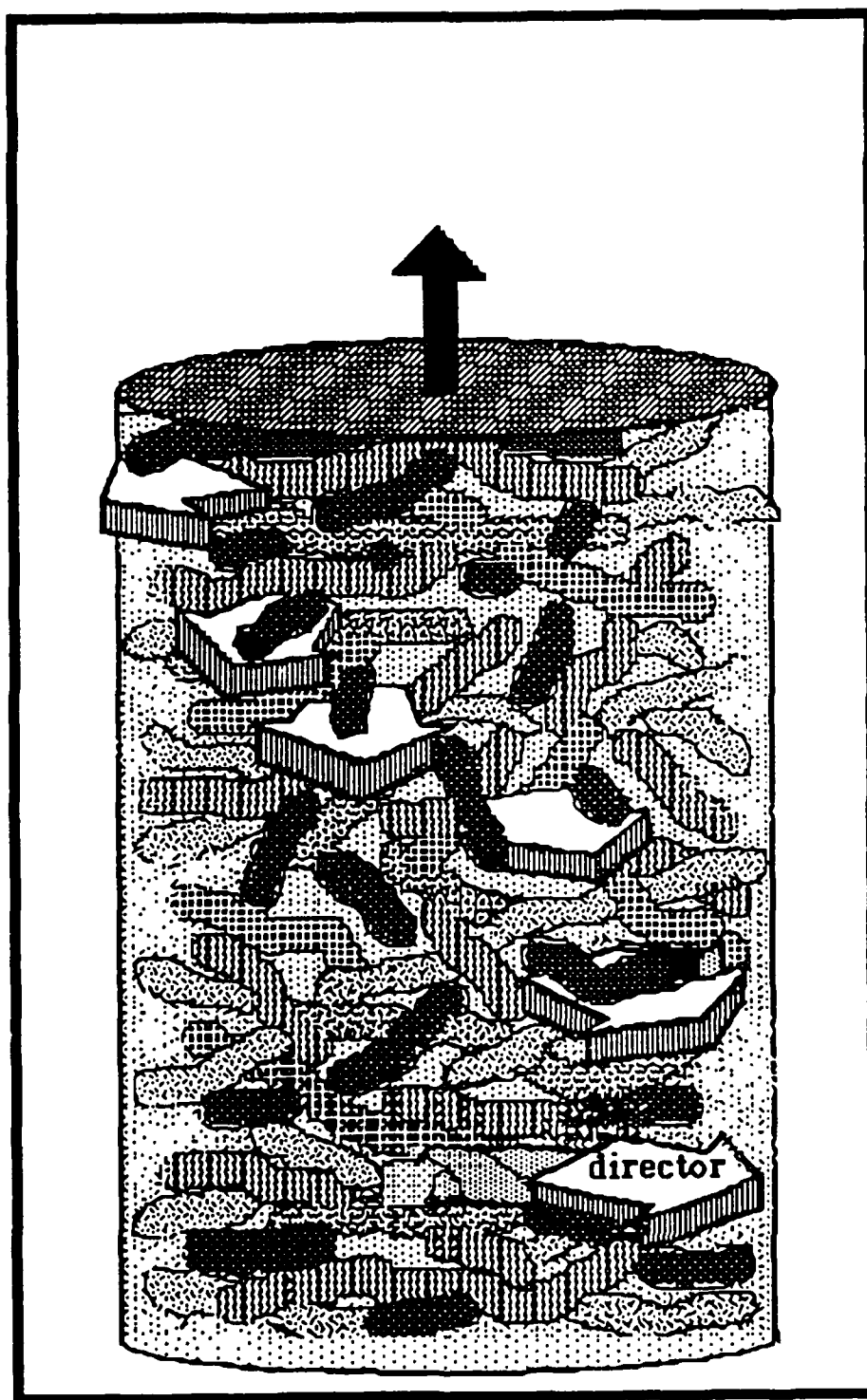
FIGURE 2.4 Helicoidal cholesteric structure in a mainchain LCP.

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MACROMOLECULAR DESIGN AND SYNTHESIS

Thermotropics

Mainchain (linear) LCPs are generally synthesized by condensation polymerization involving transesterification (Jackson, 1989) (Figure 2.5). The growth step is an acidolysis reaction yielding an ester connecting link accompanied by the loss of acetic acid. The polymerization is usually conducted in the melt, although in some cases the use of an inert suspending medium is reported. The reaction in the melt is carried out either to completion or first to low molecular-weight-oligomer followed by solid state polymerization to high molecular weight. This general approach is employed for the important high-temperature all-aromatic polymers such as Xydar® (Amoco), Vectra® (Hoechst-Celanese), Victrex® SRP (ICI), and presumably the recent polymers announced by Du Pont and Granmont/Montedison.

Polyester
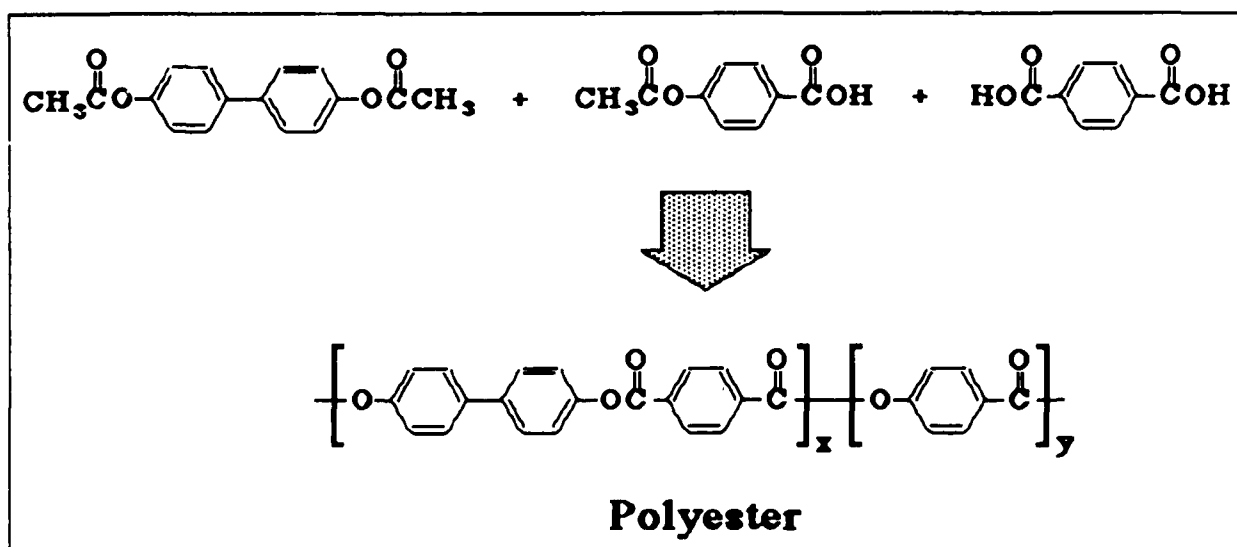
FIGURE 2.5 Condensation poly erization involving acidolysis.

In one commercial case of an aliphatic-aromatic thermotropic LCP—the lower-use-temperature polymer X7G (Eastman)—this condensation step is preceded by the reaction of acetoxybenzoic acid with poly(ethylene terephthalate) (PET) in an acidolysis reaction in which the PET chain is cleaved. This results in one chain capped with a carbophenyl carboxylic acid moiety and the other capped with an acetoxyphenyl moiety. This is then followed by the acidolysis reaction of the acetoxy and carboxyl end groups, with loss of acetic acid accompanied by other acidolysis reactions. This sequence in short rebuilds the molecular weight with accompanying insertion of oxyphenylcarbonyl mer sequences.

Typical copolyester LCPs are shown in Figure 2.6.

FIGURE 2.6 Representative potential thermotropic copolyesters.

Lyotropics

The lyotropic LCPs are prepared by solution polycondensation (Figure 2.7). For many of the extended chain polyamides, solution polymerization in amide solvents is the preferred method. For example, poly(p-phenylene terephthalamide) is synthesized by reacting the appropriate aromatic diamine, p-phenylenediamine in this case, with terephthaloyl chloride in an amphoteric solvent, such as N-methyl-2-pyrrolidone containing a solubility-enhancing salt. Lyotropic LC polyamides, depending on their composition, may be spun directly from their reaction media, or they may be isolated, redissolved, and spun from solutions containing strongly interacting acids, such as sulfuric acid, oleum, etc. The use of a phosphorylation method for the preparation of aromatic polyamides involves the direct condensation of aromatic amino acids or aromatic diamines with aromatic diacids in the presence of an aryl phosphite and organic base. Typical unit structures that yield polyamide lyotropic LCPs are shown in Figure 2.8.
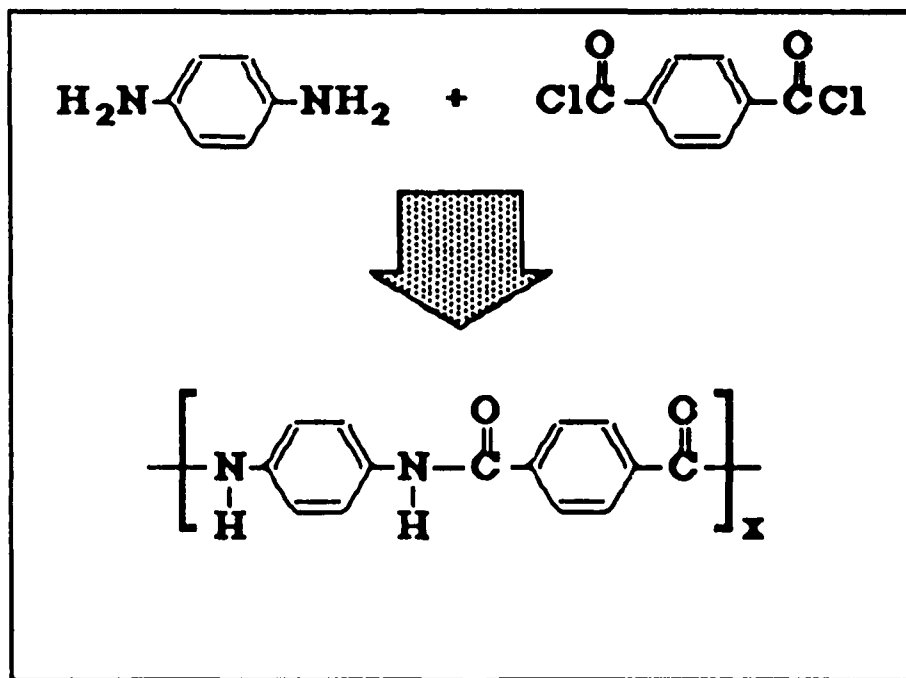
FIGURE 2.7   Synthesis of polyarylamides.

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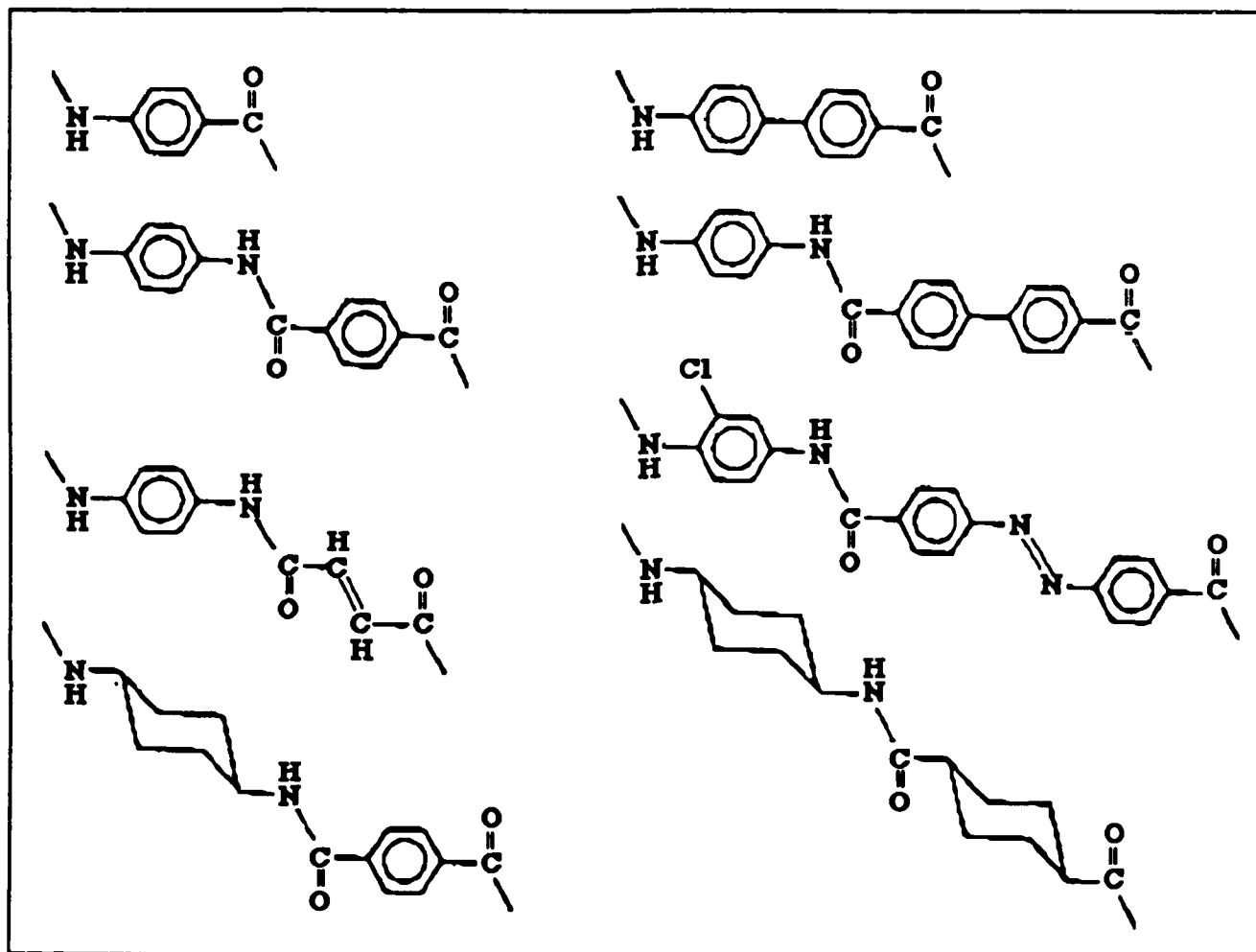
FIGURE 2.8 Lyotropic polyamide unit structures.

Poly(p-phenylene-2,6-benzobisthiazole) (PBZT) (Figure 2.9) and poly(p-phenylene-2,6-benzobisoxazole) (PBO) were initially prepared at the Air Force Materials Laboratory at Wright-Patterson Air Force Base (see Wolfe, 1988, for a review). PBZT was prepared by the reaction of 2,5-diamino-1,4-benzene-dithiol dihydrochloride with terephthalic acid in polyphosphoric acid. PBO is similarly derived from 4,6-diamino-1,3-benzenediol dihydrochloride. The procedure also works well for A-B type monomers, such as 3-amino-4-mercaptobenzoic acid and 3-amino-4-hydroxybenzoic acids (Chow et al., 1989). The preparation of "molecular complexes" from blends of polymers derived from A-A+B-B monomers and polymers derived from A-B types has also been reported (Wolfe, 1988).
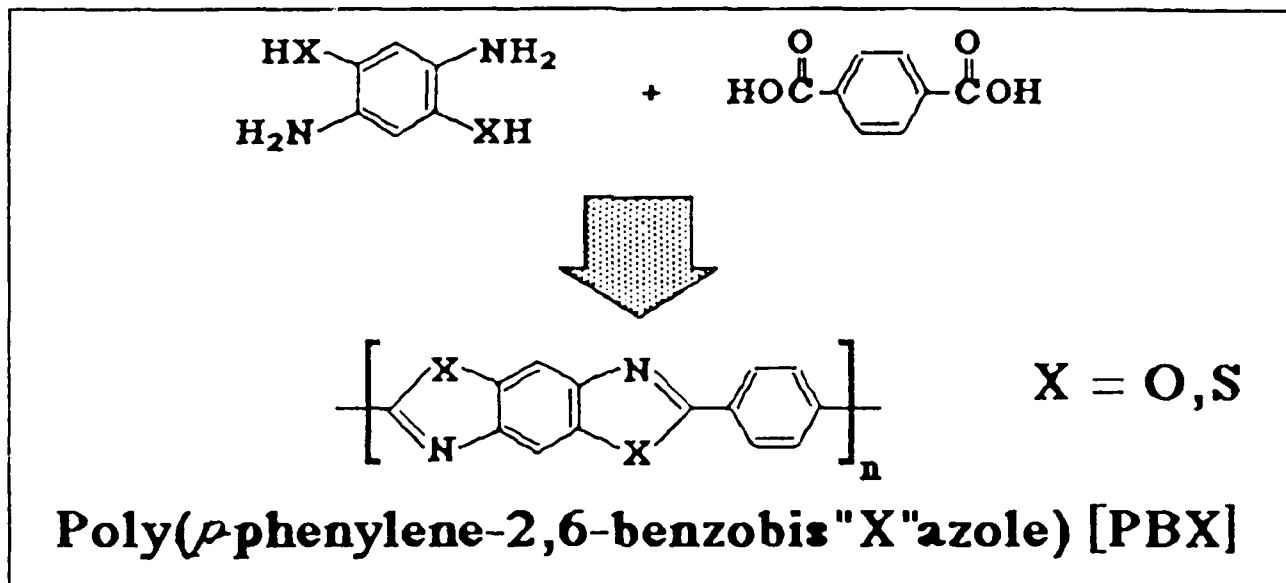
FIGURE 2.9 Synthesis of PBX polymers.

Sidechain Thermotropic LCPs

While most of the interest in LCPs is focused on mainchain polymers, an important class of LCPs contains the mesogenic groups as an appendage (mesogenic core) on the polymer—sidechain LCPs (see Attard and Williams, 1986, for a review). Synthetic routes to sidechain LCPs have traditionally involved polymerization of a vinyl monomer (e.g., acrylate or methacrylate) under free radical conditions in solution (Figure 2.10). (The only real difficulty with this reaction is encountered when radical reactive groups are located elsewhere in the monomer.)

It is also possible to produce sidechain LCPs through polycondensation. For example, malonate monomers can be converted to polyesters in a polyesterification reaction (Figure 2.11). This reaction is of special interest for radical reactive groups such as nitroaromatics and stilbenes, which have application in nonlinear optics. Polycondensation of combined sidechain and mainchain LCPs can also be utilized.
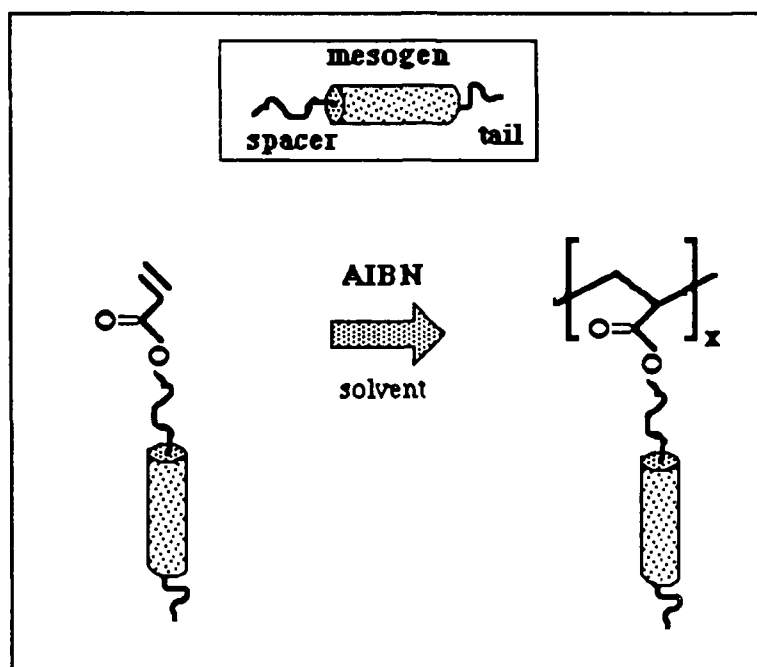
FIGURE 2.10 Preparation of sidechain LCPs by free radical polymerization.
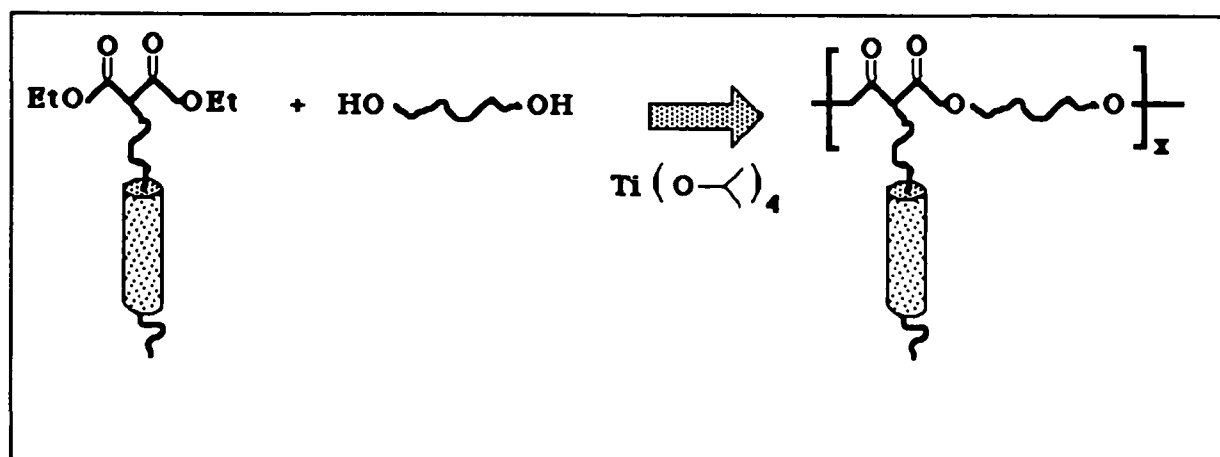
FIGURE 2.11 Preparation of sidechain LCPs by polyesterification.

Reactions on preformed polymer chains allow derivatization of a reactive polymer by attachment of a spacer and a mesogen (Figure 2.12).
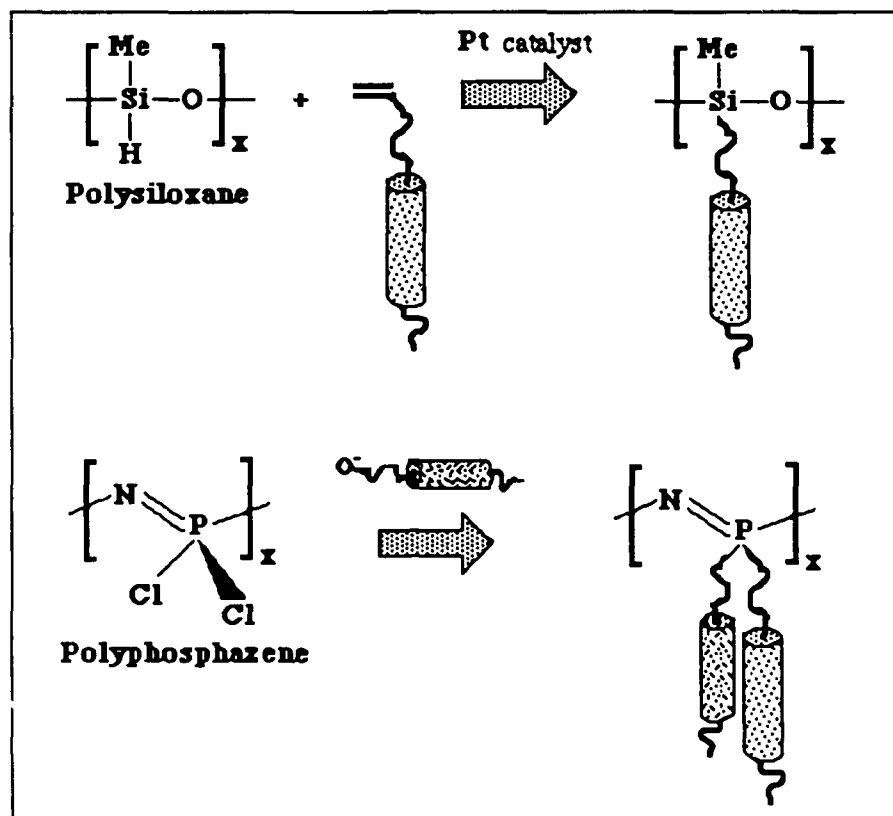
FIGURE 2.12 Examples of preparation of sidechain LCPs by derivatization of preformed polymers.

Ringsdorf and co-workers have described a variety of sidechain LCPs (and combination polymers, i.e., sidechain/mainchain mesogens together) (Ringsdorf et al., 1989, and references cited therein.) Moreover, these workers have considered oblate as well as prolate mesogenic cores. Thus far we have only considered the latter, which form conventional calamitic phases. Oblate mesogenic cores, on the other hand, form columnar phases wherein the columns may pack on a hexagonal lattice. Such lattice organizations are stabilized in the polymeric forms of these oblate mesogens. These ordered arrays of columns present an interesting and unique state of order in the LC and solid state of organic polymers.

Sidechain Lyotropic LCPs

For completeness we note that there are examples of sidechain lyotropic LCPs wherein the mesogenic unit is amphiphilic (Finklemann, 1987). There are also recent proposed structures of combination LCPs that are derivative of lyotropic (non-amphiphilic) rigid-rod polymers (Dowell, 1989).

UNDERSTANDING AND THEORY

Order-Disorder Transitions in Polymer Fluids

For polymers, the influence of molecular anisometry on the propensity of mesophase formation has been explained mainly on the basis of intermolecular and intersegmental repulsion—i.e., steric or excluded volume effects (Flory, 1984; Matheson and Flory, 1981). For the case where no attractions are acting between chains and where the chains are perfectly rigid rods, a statistical thermodynamical theory was formulated (Onsager, 1949; Flory, 1956) more than 40 years ago that laid the foundation for much experimental work in lyotropic systems and for more advanced theories. Today, this is known: For rigid noninteracting rod-like chains in solution, there exists an isotropic phase at low concentrations and an anisotropic phase at high concentrations, with a concentration range of stable biphasic equilibrium in between. The threshold volume fraction v_p* for the appearance of an anisotropic phase is approximated by

$$v_p* \approx (8/x) \ [1-(2/x)]$$

where x is the aspect ratio of the chain. (The aspect ratio is proportional to the molecular weight and can be calculated from estimates of the bulk density and the length and orientation of the constitutional repeat unit. In fact, it is the chain's persistence length that is relevant for the computation of x.) Interacting rigid rod-like chains behave somewhat differently, but this difference becomes gradually insignificant with increasing molecular weights (Flory and Ronca, 1979).

Semiflexible chains are highly extended molecules with significant flexibility that nevertheless impart, unlike their flexible random coiling counterparts, the potential for the formation of anisotropic phases to their solutions and melts. For polymers with a uniform (and small) degree of flexibility along the chain, the "worm-like chain" model is appropriate; thermotropic and lyotropic systems can be interpreted with this model. Polymers that consist of rigid segments joined by flexible spacers can be treated by appropriate modification of the individual rigid rod molecule approach (Boehm et al., 1986), and, if the spacers are sufficiently flexible joints and the rods sufficiently long, they behave roughly as if they were independent (Flory, 1984).

Mesomorphic Textures and Structures

Mainchain LCPs contain microstructures in their melts and solutions on both a micrometer and a submicrometer scale. The most prominent feature, undoubtedly because it can be observed using optical microscopy, is the micrometer-scale "domain-like" structure, which is a manifestation of high local molecular orientation. These optically defined domains observed in LCPs are regions of nearly uniform director orientation. The domain-like texture is unlikely to represent an equilibrium texture and is not predicted by any available theory. The character of the submicrometer boundaries between these apparent domains has not been well characterized; they may consist of strained nematic fluid with some disclinations (the analogue of dislocation faults in a

crystal; see, for example Thomas and Wood, 1986) or of more mobile fluid made up of chain ends or of isotropic fluid of different composition from the bulk (or both) (Nicely et al., 1987; Amundson et al., 1987).

Heterogeneity on macroscopic levels is also observed. Lyotropic systems have a biphasic concentration range leading to bulk separated isotropic and LC phases. Although most thermotropic melts that have been studied appear to be uniformly mesogenic on all scales, there are exceptions. The copolyester of 60 mole percent p-hydroxybenzoic acid and 40 mole percent poly(ethylene terephthalate) has been widely studied and is multiphasic with an isotropic component of different composition from the mesophase. Terminology derived from semi-crystalline polymers—degree of liquid crystallinity—is sometimes used to describe such heterogeneity. However, this terminology is complicated. For example, some thermotropic melts that have been characterized rheologically also appear to contain a small fraction of actual crystallites with dimensions of the order of 100 Å at the temperatures at which processing is normally carried out (Amundson, 1989; Kalika et al., 1990; Lin and Winter, 1988). These crystallites affect the flow, and they are one likely cause of the observed sensitivity of melt rheology to thermal history. (Large thermal history effects on rheology may also be a consequence of annealing textures [reorganization of domains] or, in some cases, chemical reaction occurring during physical characterization, including decomposition, polymerization, and transesterification.)

Rheology

The flow of LCPs is affected by the textures described above in a variety of ways. Moreover, the flow itself changes the microstructure. Nevertheless, idealized descriptions of (assumed) homogeneous mesophases are useful to gain insights into flow behavior. Continuum theories of LC rheology developed for low-molar-mass nematics relate the stress at a point to the deformation and director field and contain a description of the dynamics of the director field in terms of the director, stress, and deformation field (Ericksen, 1977; Leslie, 1979).

Shear flow appears to have little effect on macroscopic director orientation, either experimentally or in the context of continuum theories for anisotropic liquids, but flows with an elongational component are very effective. This is the reason unidirectional orientation (fiber formation) is achieved easily in LCPs. Typical flow in molds contains regions of extensional deformation (in the "fountain flow" near the moving front, for example), so high degrees of orientation are achieved in some "skin" regions of a molded part. The high degree of orientation translates into anisotropic mechanical properties. Flow in molding can lead to regions of rapid change in macroscopic director orientation including high transverse orientation in the core (Field et al., 1988). The effect can be analogous to layering of unidirectional sheets. Often the "self-adhesion" of these sheets is poor, resulting in poor lateral strength (delamination).

Theory

In molecules of low molar mass with mesogenic properties, the molecular anisometry must be appreciable; this asymmetry of shape is a prerequisite for substances to exhibit liquid crystallinity and has been convincingly interpreted (Flory, 1984; Chandrasekhar, 1977; and De Gennes, 1971). In addition, intermolecular attractions, especially those strongly dependent on the mutual orientation of the molecules, play a role, but they usually contribute less toward the development of a liquid crystalline phase.

Rod-like polymers, or chains with very limited flexibility and a more-or-less linear trajectory, pervade much more of space than their flexible random trajectory counterparts; i.e., they have much larger radii of gyration. The radius of gyration for a random coil with molecular weight M varies as $M^{0.5}$ at the theta point and as $M^{0.6}$ in a good solvent; it is proportional to M for a rigid rod. As a result, rigid rod-like chains strongly interact with each other at much lower concentrations than flexible polymers do. This is reflected in, for instance, by the large dilute solution viscosity, the large relaxation times, and the small diffusion coefficients exhibited by rod-like chains. Above a threshold concentration, the strong interactions produce a mutual orientation about a common local director; this in turn allows for easy orientation of the rod-like molecules by external influences (e.g., an electric or magnetic field, a shear field), which facilitate processing of such materials into products of well-defined orientation—one of the prime attractions of LCPs. The physical and the transport property differences between random coil and rigid rod polymers increase with increasing concentration, but so do the theoretical difficulties associated with describing their behavior.

PROCESSING

Solid structures that benefit most from the rod-like molecular structure of LCPs are uniaxial. Easy orientation in the flow field and resistance to chain folding on solidification lead to fibers with outstanding tensile properties. LCP fibers have a very high specific strength and modulus. In addition, some of the LCP fibers exhibit the outstanding temperature performance required for aerospace applications. In this section we consider processing routes to solid LCPs via both thermotropic and lyotropic phases.

Thermotropic LCPs

The commercial utilization of thermotropic LCPs is a direct function of the ability to process these polymers into cost-effective solid parts. Paramount for achieving this is the understanding and reduction to practice of methods to control molecular orientation in three dimensions. Historically, orientation in polymers has been introduced mechanically. Except for the production of uniaxial shapes with at least one thin dimension (about 40 μm or less), orientation is difficult to control in LCPs. Injection molding, while successful in producing useful and even unique parts, does not allow

exploitation of the LCP mechanical property potential. Weak weld lines permeate molded parts. They are due to the lack of molecular mixing across flow-induced interfaces separating director fields with different relative orientations. These "grain" or domain boundaries present a significant problem with complex molded shapes. Orientation-inducing processing techniques other than mechanical (for example, the use of surface epitaxy, electromagnetic fields, or "crystallization templates") may prove to be effective new directions for the production of LCP parts and devices with controlled orientation and stronger weld lines. The potential of new approaches such as cold-forming processes (see Chapter 4) needs to be assessed both in terms of technical feasibility and added manufacturing costs.

Lyotropic LCPs

Although the formation of liquid crystalline solutions by extended-chain, rod-like polymers has been noted in at least ten classes of polymers (Kwolek et al., 1987), only aramids and ordered aromatic heterocyclics have been extensively examined with respect to LCP-induced, unique solid-state properties. Here we focus on these two classes of polymers as fiber- and film-forming polymers. Kevlar® aramid polymer has been manufactured by the Du Pont Company since the early 1970s (Kwolek, 1980), while rigid aromatic polybenzobisoxazoles (PBO) and polybenzobisbisthiazoles (PBZT) are currently under consideration for commercialization.

Fibers

The ability of extended-chain, rod-like polymers to form lyotropic (nematic) mesophases under certain conditions (molecular weight, solvent, concentration, and temperature) is critical to their processing into solid parts. Uniaxial solid fibers dominate the commercial utilization of lyotropic LCPs. For example, spinning lyotropic solutions can result in fibers with very high strength and very high modulus and with nearly perfect orientation **without** subsequent mechanical processing, i.e., without stretching the extruded and solidified fibers. With these otherwise intractable polymers, such fiber properties have not been achieved by other means.

Selection of a spinning method (dry, wet, or dry jet-wet) is determined primarily by the polymer-solvent system and economic considerations. For example, Kevlar® aramid fiber utilizes a dry jet-wet spinning process. The highly ordered nematic phase in a solution with greater than 18 weight percent of high-molecular-weight poly-p-phenyleneterephthalamide (PPTA) in approximately 100 percent sulfuric acid is retained and perfected by elongational forces in the air gap, and by further drawdown in the coagulating medium. The high (as-spun) chain orientation is directly related to the high fiber tenacity (> 20 gpd) and high (approaching theoretical values after heat treatment) modulus. Spinning conditions for lyotropic aramids and structure-property relationships of the resulting fibers have been studied extensively and are described in patents and literature reviews (see, for example, Schaefgen, 1983; Jaffe and Jones, 1985; Schaefgen et al., 1979; Preorsek, 1982; Dobb, 1985; and Kwolek et al., 1988). Subsequent heat treatment of

these fibers under tension (but with practically no draw) at 150 to 550°C can result in further improvement of tensile properties and orientation. The heat treatment response is dependent on the structure and molecular orientation of the as-spun fibers and on the method of spinning. Since thermal polycondensation of aromatic diamines and aromatic diacids is at best very slow, the increase in tenacity and modulus upon heat treatment is attributed to increased orientation and crystallization of the polymer chains.

Similar findings apply to solid fibers fabricated from polymeric aromatic heterocycles. Since PBZT and PBO are soluble only in strongly interacting acids, fiber formation involves removal of the acid solvent and rapid coagulation of the polymer by a nonsolvent, such as water. As with Kevlar®, the optically anisotropic PBZT or PBO-polyphosphoric acid solutions are dry jet-wet spun into fibers with ultrahigh tenacity and ultrahigh modulus. Polymer preparation in polyphosphoric acid, spinning conditions, and fiber properties of these extended-chain rigid heterocyclic polymers are described in a number of patents and literature reviews (Wolfe, 1988, and references cited therein). Heat treatment is similar to that of aramids except that the temperature range is from 375 to 690°C. There is a wide range of properties, depending on processing conditions.

Films

The very limited published material on films from fabricated lyotropic polymers may indicate that wet extrusion does not lend itself easily to film formation. Films produced from anisotropic PPTA-sulfuric acid solutions (by wet or dry jet-wet extrusion with uniaxial drawdown) exhibit polymer orientation in the machine direction and highly anisotropic mechanical properties. PPTA films produced with a lubricated conical mandrel between the die and the coagulating bath exhibit equal biaxial orientation and balanced properties. Although heat treatment at 350°C of the latter films results in a significant enhancement of tensile properties and a reduction in voids, these improved properties are very inferior to those of the corresponding fiber (Bodhagi et al., 1984). Flood and Fellers (1987) have used mandrels of conical, hyperbolic and ogival shapes to obtain a high degree of biaxial chain orientation in PPTA films. Molecular orientation as well as mechanical properties were found to be dependent on mandrel shape and presence. Tensile strength and Youngs modulus were on the order of 30 Kpsi and 1 Mpsi (0.21 GPa and 6.9 GPa), respectively versus 400 Kpsi and 9 Mpsi (2.8 GPa and 62 GPa) for Kevlar® 29 fiber. Biaxial films appeared to be more homogeneous compared to uniaxially drawn films. Films prepared from PBZT-polyphosphoric acid solutions by dry jet-wet extrusion also have high axial orientation and high unidirectional properties (tensile strength and modulus of 1.5 and 240 GPa, respectively, after heat treatment) but poor properties in the transverse direction (Feldman et al., 1985). Also, like other anisotropic films, they exhibit axial splitting. More recently, biaxially oriented films of PBT have been prepared by the use of a specially designed die that allows for biaxial orientation to occur during extrusion of the PBZT-polyphosphoric acid solution (R. Lusignea, presentation to the committee).

Solid-State Forming

Novel processing of thermoplastics can be defined in many ways but for the purposes of this report will be considered to mean any forming method conducted at temperatures at or below the melting point (solid-to-mesomorphic transition) of the LCP. While such processes are widely used for many semicrystalline polymers, they account for far less volume than traditional melt-processing. In the case of thermotropic LCPs, the sintering process was one of the first to be applied to the hydroxybenzoic acid polymers introduced by the Carborundum Company (Economy et al., 1970a and 1970b; Economy, 1989). However, the exploitation of these techniques has not been noticeable against the rapid growth in, for example, the injection-molding area.

The explanation for this is probably not in the behavior of the LCP material itself, relative to random-coil, semicrystalline polymers. However, relatively little information is available to support the hypothesis that the LCPs can be solid-state formed with the same ease as conventional polymers. The empirical criterion of Aharoni and Sibilia (1978) that a crystal-crystal transition must exist may not apply in the case of rigid rod molecules, although such transitions are thought to be quite common (Field et al., 1988; Hsiao et al., 1988). It should be noted that transitions that could lead to mobility in the crystals may be induced at high hydrostatic pressure; thus some forming processes could succeed while others may fail. Table 2.1 illustrates the more common solid-state forming methods (Shaw, 1980). It should be remembered, on scanning this table, that many commercial fabrication processes involve two or more of these, either in sequence or, in effect, simultaneously. For example, the combination of coining and extrusion will yield a decorated container in one step. Also, the mandrel technique has been examined but the results have not been outstanding; modulus values are one to two orders of magnitude below Kevlar® 29 (see previous section).

Many of the advantages of solid-state forming result from the avoidance of the penalties of heating a polymer to a high temperature. These penalties include energy costs, time required for cooling, large volume changes, and degradation. For many high-temperature LCPs, the latter may be the most compelling. In addition, it is possible to introduce a high degree of orientation via solid-state forming, and thereby a substantial improvement in strength. The high optical clarity of cold-formed semicrystalline polymers is often cited as an advantage, but it is not known if this will prevail for LCPs.

MECHANICAL PROPERTIES

Solid State Morphology

The focus herein is on fibers because morphological data on more complex geometries are incomplete. When one tries to analyze the molecular criteria for a perfectly aligned uniaxial system, it is not directly applicable to fibers because of a fiber's fundamental morphological characteristics.

TABLE 2.1 Cold-Forming Methods for Polymers

Process	Typical Products	Closest Simple Deformation	Schematic
Cold drawing	Fibers, tapes, rods	Uniaxial extension	
Bending	Angles, channels	Pure shear	
Cold extrusion	Rods, tapes	Uniaxial extension	
Hydrostatic extrusion	Rods, tapes	Uniaxial extension	

TABLE 2.1 Cold-Forming Methods for Polymers (continued)
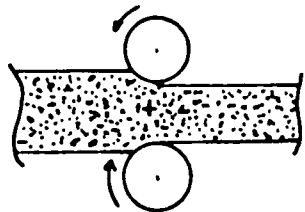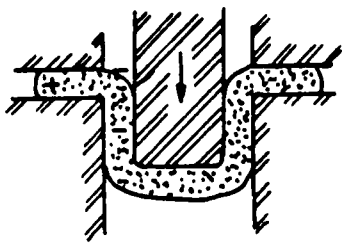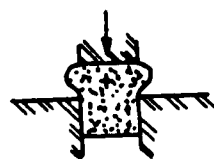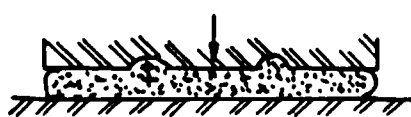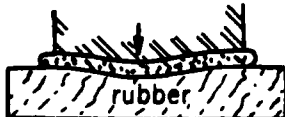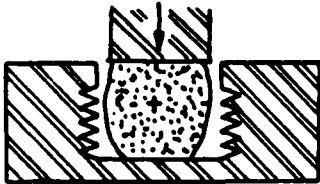
Process	Typical Products	Closest Simple Deformation	Schematic
Rolling	Sheet, tapes	Pure shear	
Deep drawing (draw forming stamping)	Cups	Pure shear	
Upsetting (cold heating)	Knobs, nails	Compression	
Matched-die forming (stamping)	Various	Pure shear	
Coining	Raised Letters		

TABLE 2.1 Cold-Forming Methods for Polymers (continued)

Process	Typical Products	Closest Simple Deformation	Schematic
Hydroforming	Cups	Biaxial extension	
Rubber pad forming	Cups		
Stretch forming	Cups	Biaxial extension	
Forging, cold molding (compression molding)	Gears, pulleys		

Conventional fibers derived from ordinary semicrystalline polymers are a complex aggregate of strong, highly ordered microfibrils and macrofibrils that are usually separated by a weak boundary (Peterlin, 1979) (Figure 2.13). Therefore, polymeric fibers tend to fibrillate or split into these subelements when bent. Although there are many ways to produce fibers, the final products always exhibit a well-developed fibrillar substructure. Moreover, this tendency toward fibrillation appears to be exacerbated in fiber derived from LCPs, even though extended-chain crystal habits as opposed to thin lamellar crystallites (see inserts in Figure 2.13) prevail in these new polymers (Sawyer and Jaffe, 1986).
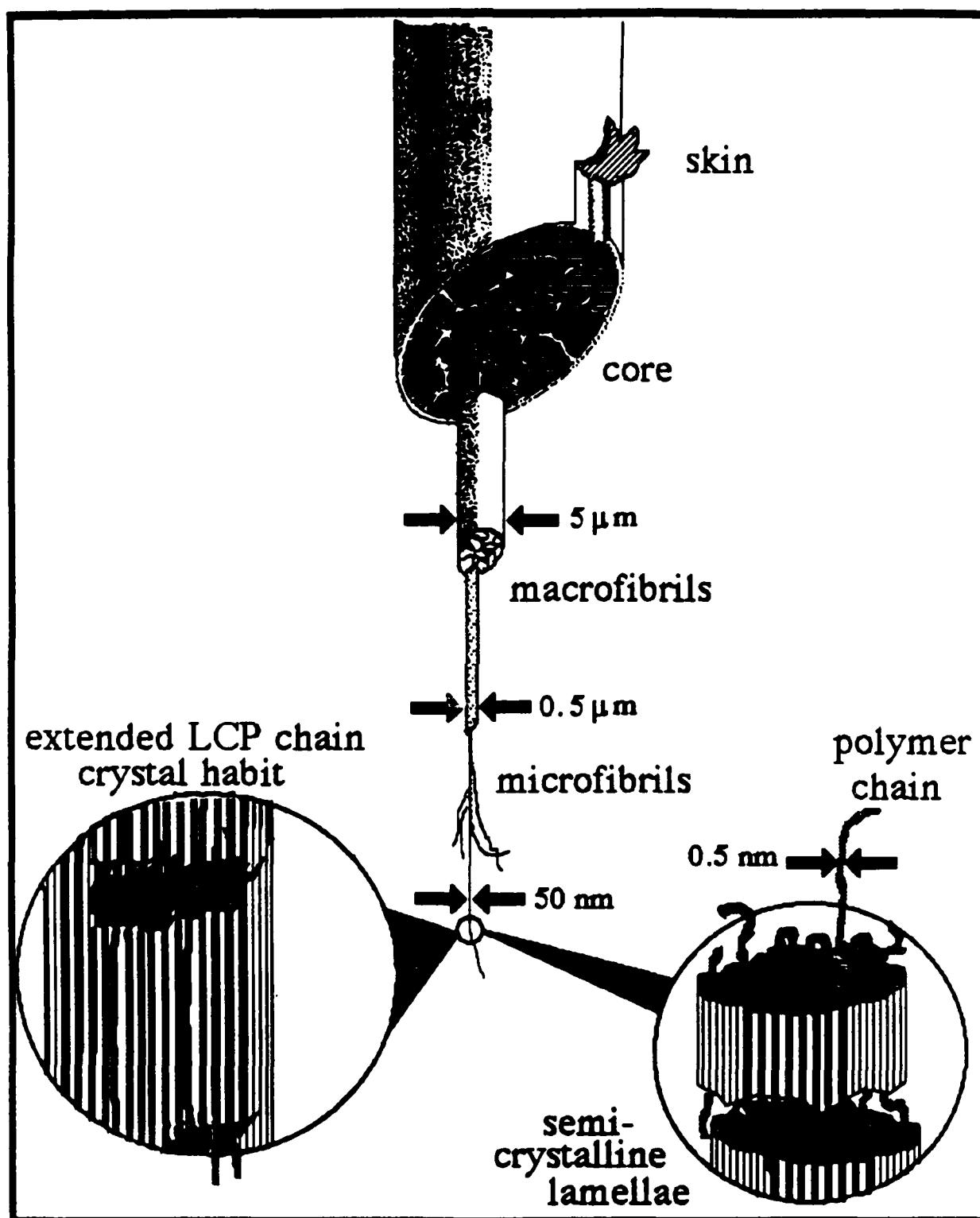
FIGURE 2.13 Hierarchical morphology in fibers.

Since the interfibrillar domains are weaker than the fibrils, it is necessary to determine the consequences of fibrillar structure and interfibrillar strength on tensile and compressive properties. An extreme case where the interfibrillar domains are very weak and their volume fraction is approximately 0.25 illustrates the role of interfibrillar strength in tension and compression. Note that, regardless of the lateral dimensions of the microfibrils, the properties in tension would in this case amount to approximately 75 percent of the fibrillar strength. The compressive strength, on the other hand, depends on the cross-sectional area of the microfibril and approaches zero as the macrofibril gets thinner.

In tension, the most important factors controlling the strength are the strength of the weakest bond of the molecule and its cross-sectional area. The stronger the individual polymer chain and the smaller its cross-sectional area, the higher is the theoretical strength of the ensemble of perfectly aligned molecules. The interactions between the molecules are of secondary importance and affect only the molecular weight dependence of strength (Termonia and Smith, 1988; Prevorsek, 1988).

In compression, the key factors are the torsional and bending rigidity of the molecule and the interactions between adjacent molecules (DeTeresa et al., 1985). The effect of the cross-sectional area in compression is opposite to the effect in tension. Molecules with large cross-sectional areas usually offer a higher potential for compressive strength. Consequently, a polymer molecule designed for optimal performance in tension will generally exhibit low compressive strength, and vice versa.

When the molecular criteria are taken into consideration, the following ranking of fibers with respect to their <u>increasing</u> compressive strength potential is obtained:

> PE < thermotropic polyesters < rigid rod polymers (PBZT, PBO)
> < aramids < PVA < carbon fibers

Note that polyethylene (PE), with the highest achieved strength in tension, is the lowest on this compressive strength scale, and that the aramids are above thermotropic and rigid-rod polymers because of their proclivity for interchain hydrogen bonding. Poly(vinyl alcohol) (PVA) fibers are a step beyond aramids because of the higher hydrogen bond density. The compressive strength of carbon fibers is high because of their large cross-sectional area and sheet-like structure of the macromolecule.

Very recent work on compressive strength of ultra-strong PE fibers and their composites, along with the work on strain rate dependence of PE fiber properties raises the question whether the reported very low compressive strength should be attributed to a specific PE fiber or whether it reflects a true inherent characteristic of uniaxial fibrous PE.

The uncertainties exist for the following reasons:

1. The commercially available ultra-strong PE fibers have irregular, frequently flattened cross-section

2.   On a close inspection, these fibers already show before testing, some compressive damage (kink bands), and

3.   Poor adhesion between the PE fiber and various rigid matrices.

The first two issues preclude a straightforward determination of the compressive strength for fibers, and the latter from composites. It has been observed that even with the most effective treatments, the fracture path in PE fiber composites never traverses the fibers as is the case in Kevlar® fiber composites, but follows the fiber-matrix interface.

In addition, PE exhibits well known strain rate dependence of mechanical properties. While the creep phenomena of PE were well researched and documented, the strain rate effects at very high rates of deformation were discussed only very recently. Recent studies (Prevorsek, 1989) confirmed the expectation that compressive and tensile properties of PE increased with increasing rate of deformation. This includes the compressive strength and modulus that at the rate of ballistic events and high speed impact appear to exceed the properties of aramids.

BLENDS AND COMPOSITES

The intimate mixing of two or more polymers to form a new material with a unique property set has emerged as a desirable route to new product development. The resulting blend or alloy (the terms are usually equivalent), if consisting of commercially available polymers, greatly reduces the time and costs associated with new materials development while offering the possibility of a low-cost product with tailored properties and/or improved processibility. Miscible (thermodynamically compatible) blends form a single homogeneous phase and offer the potential for control of transition and processing temperatures. Properties tend to follow the "rule of mixtures" but, synergies are not uncommon. One significant commercial example of a miscible polymer blend is the polystyrene-poly(phenylene oxide) system developed by GE.

Phase-separated (thermodynamically incompatible) blends are much more common, with "rubber-toughened" thermoplastics the most common and successful in this class of materials. Phase-separated blend technology is an effective method for modifying a key resin property (most often toughness) while leaving the majority of resin properties unchanged. The efficiency of property modification is a function of the nature of the dispersion of one polymer in the other (size, geometry) and the degree of adhesion between the phases. If there is sufficient interaction between the blended polymers to cause transition temperatures of the polyphasic system to shift and/or the adhesion between the polymers to improve, the polymers are "partially compatible." So-called compatibilizing agents are third components, often of low molecular weight, added to immiscible blends to augment dispersion of the included phase or adhesion between the phases. (Note the term "compatibilize" is often loosely employed by technologists to denote "fine dispersion" of one polymer in another one brought about by adding a third component.)

Interpenetrating network (IPN) is the term used to define co-continuous phase morphology (often intimately mixed thermosets). If a thermoset is cross-linked in the presence of a thermoplastic, the system is described as a semi-IPN. If one phase orients during processing such that the matrix resin is reinforced, the system may be described as an "in situ composite" or a "self-reinforcing polymer." "Molecular composite" is the term used to describe a molecular dispersion (ideally) of rigid rod polymers (e.g., PBZT) in a conventional polymer matrix (Wang et al., 1988).

Molecular Composites

The concept of molecular composites may be appreciated in the evaluation by Flory of ternary systems consisting of (a) the polymer rod (single macromolecule of the PBX type, aramids, copolyesters, etc.), (b) the conventional (random coil) polymer, and (c) the solvent. The evaluation predicts that a critical region will exist wherein there is a single isotropic phase consisting of rods randomly dispersed in the coils. This region is very narrow in its stability boundaries, and the retention of this structure in the solid state depends on "beating the kinetics." Hence, if phase separation can be avoided on solidification, given the extraordinarily high mechanical properties of the individual macromolecular rods, products (including fibers) with excellent tensile and compressive properties should result (a significant fraction [1/3] of rods in such a solid is always in tension). If the composite material could be fabricated into three-dimensional parts, these parts would likely possess the high level of specific mechanical properties currently achievable with LCP-derived fibers and would be extremely attractive for aerospace applications.

Many of the motivations for blending LCPs with conventional polymers or with other LCPs are the same that generally make blending an attractive polymer modification option. These motivations include cost reduction, property tailoring, accelerated new-product development, and improved processibility. (Improved processibility focuses on utilizing the low viscosity of the LCP to improve the processibility of highly viscous conventional resins.) The cost-reduction objective is to provide an LCP-like property set at appreciably less than "pure" LCP property prices. Property tailoring is attractive from two points of view: First, with conventional polymers, LCPs can function as a high-modulus fibrous (macroscopic) reinforcement, and, second, with other LCPs or at relatively low levels of conventional polymer addition, the objective is to mitigate LCP problems such as poor weld line strength or high anisotropy of properties. If a commercially useful family of LCP-containing resins can be defined, the rapid increase of new LCP-containing products will naturally follow. Finally, the blending of LCPs with other LCPs provides useful data for studying the nature of the structure, morphology, and chain-to-chain interactions in these new LCP materials, while offering the opportunity of improved property sets (DeMeusse and Jaffe, 1988).

ELECTRO-OPTICAL PROPERTIES

Herein the focus is on nonlinear optical (NLO) properties of organic systems involving LCPs. There are, however, a number of recent phenomena (generally linear electro-optic) that employ conventional polymers or LCPs together with low-molar-mass LCs. The latter (guest) is dispersed in the host polymer matrix as a microemulsion and the director responds to an applied field thereby changing the refractive index difference between the guest LC and polymer (LCP) host. The phenomena may be adapted to light attenuation and optical switching (Doan et al., 1986; Drzaic, 1986). In the cases of NLO phenomena, readers may readily sense the intensity of interest in organic polymeric systems, in general (Boyd, 1989), and in LCPs (Williams, 1987), in particular.

Relevant aspects of second- and third-order NLO processes are reviewed here so that readers may consider the potential of LCPs in this active research area, one that is anticipated to yield technologically important advances in the future (Williams, 1987).

Second-Order NLO Processes

There are basically two categories of second-order NLO processes: (a) the linear electro-optic or Pockels effect and (b) parametric processes such as second-harmonic generation (SHG) and sum or difference frequency generation. In the former a d.c. electric field is applied to a medium, which responds by altering its refractive index in proportion to the applied field. In the latter the electric field associated with incident light produces polarization components at other frequencies, which can act as a source of electromagnetic radiation at those frequencies. For a material to exhibit significant second-order NLO responses it must have a noncentrosymmetric structure. In the case of polymers this implies that a polar symmetry axis must be introduced into a medium that would otherwise be nonpolar because of orientational averaging. Electric field poling of thermoplastic polymers at elevated temperatures (above the glass transition temperature, T_g) leads to the introduction of a polar axis (by biasing molecular dipoles in the direction of the applied field) (Meredith et al., 1982; Le Barny et al., 1987; DeMartino, 1988). This induced polarity can be retained by cooling the polymer to well below its T_g. The main advantage of introducing liquid crystallinity into polymers for second-order NLO applications is the enhancement in the degree of polar molecular alignment it can provide; up to a factor of 5 under certain processing conditions. The origin of this enhancement is the effect of the local anisotropic potential associated with the liquid crystalline director on the orientational distribution function of the nonlinear chromophore. Enhanced alignment translates into up to a factor of 5 larger nonlinear coefficient, which in turn can increase the efficiency of processes such as second-harmonic generation by over an order of magnitude. For third-order NLO materials uniaxial alignment associated with the liquid crystalline director can have a similar enhancement in the coefficient by removing the spatial averaging effects of an isotropic environment on the direction of largest nonlinearity in the chromophore. For commercial applications the stability of retained alignment is of primary concern since

critical device characteristics are determined by the stability of parameters related to alignment. Liquid crystallinity can assist in the retention of local alignment because of its highly anisotropic contribution to the local orientational potential energy (D. J. Williams, 1987).

An alternative approach to inducing noncentrosymmetry might be to introduce chirality and the other structural requirements of the ferroelectric smectic c* mesophase into a polymeric structure containing chromophores capable of producing a nonlinear response (Goodby and Leslie, 1984). Because of its complexity, this approach has not yet been fully examined or exploited, but it may be fruitful for achieving high degrees of order with excellent stability.

Most devices designed to take advantage of the Pockels effect operate by retarding the phase of light propagating through the medium with the field-induced refractive index change. One figure of merit (FOM) quantifying the suitability of a material for a particular electro-optic or integrated optic application (Alferness, 1982) is

$$\text{FOM} \propto \chi^{(2)}/n(\varepsilon + 1)$$

where $\chi^{(2)}$ is the first nonlinear coefficient, n the refractive index, and ε the dielectric constant of the electro-optical material. This FOM determines the trade-off between the electric field and path length required to achieve a particular degree of phase retardation. For very-high-speed devices where electric fields are applied via microwave transmission lines, an additional factor emerges. Here the velocity of the microwave pulse $V_m - C/\varepsilon^{\frac{1}{2}}$ must match that of light, $V_e - C/n$, in the medium over the interaction length required for a given amount of phase retardation to occur (DeMartino et al., 1987). From these considerations a large refractive index would favor phase retardation. For high-bandwidth devices operating in the traveling wave mode, n^2 approximately equals ε of the electrodes at optical frequencies. For electro-optic materials such as $LiNbO_3$, n^2 and ε are very different, so that velocity matching can only be achieved over short distances (Lytel et al., 1988). From a device design point of view, if the phase retardation must be achieved over short distances, much higher voltages are required. A thorough discussion of device-dependent requirements for electro-optic materials is beyond the scope of this report, but a general list of requirements and desirable characteristics compared to the properties of currently existing materials is presented in Chapter 3.

For second-harmonic generation, a separate FOM is required that leads to additional desirable material characteristics. Consider the fraction of power converted to the harmonic frequency, $P(2\omega)/P(\omega)$, over a certain region in a crystal. It is proportional to the following factors:

$$P(2\omega)/P(\omega) \propto [\chi^{(2)^2}/n^3(\mu/\varepsilon)^{3/2}] \cdot P(\omega)L \cdot f(\Delta kL/2)$$

where n, μ, and ε are, respectively, the refractive index, dipole moment, and dielectric constant of the nonlinear materials, and $f(\Delta kL/2)$ is a phase mismatch factor that is periodic in character and whose amplitude is reduced by increasing periodicity. The periodicity of this function is determined by

the mismatch in momentum Δk of the fundamental and harmonic waves. A FOM for harmonic conversion is given by

$$\text{FOM} = (\chi^{(2)})^2/n^3(\mu/\varepsilon)^{3/2}$$

Here it is clear that low-refractive-index materials have a considerable advantage relative to high-index materials, and the quadratic dependence of power conversion efficiency on $\chi^{(2)}$ puts a tremendous premium on that factor. The input power $P(\omega)$ and interaction length L are parameters to be played off against the material FOM. Other factors such as birefringence and geometrical optical factors limit the length over which the interaction can be maintained.

In waveguided structures designed for optimized propagation of fundamental and harmonic fields, the dependence on interaction length L becomes quadratic, and optical fields can be propagated over long distances, leading to high conversion efficiencies (Zyss and Chemla, 1987). Because of the lack of materials with suitable properties, as well as processes to fabricate them into suitable waveguides, the potential technological advantages of waveguide SHG have yet to be realized.

Third-Order NLO Processes

Third-order nonlinear processes arise from the nonlinearity in the polarization response of all dielectric media, including conjugated organic systems. The π-electrons in conjugated organic systems, being loosely bound, contribute much more strongly to the nonlinear response than the more tightly bound core electrons (Rustagi and Ducuing, 1974). Third-order processes fall into two basic categories. The first is analogous to the Pockels effect, where the refractive index change is quadratically dependent on the applied field, which can be at d.c. or optical frequencies. This can lead to a variety of interesting effects that are manifested in various device designs, including bistable switches, power limiters, and optically driven modulators (Stegeman et al., 1988). The second category of processes involves the interaction of optical fields at different frequencies, where energy can be exchanged between field components in a manner similar to second-order parametric processes. The fields can all be at the same frequency (in contrast to second-order processes, where one of the fields must be at the harmonic, sum, or difference frequency) or at different frequencies. Third-harmonic generation, degenerate four-wave mixing, and real-time holography are examples of such effects (Shen, 1984). If one of the frequencies or any combination of them matches a resonant process in the molecule or medium, large enhancements in nonlinear response can be achieved. In this case dissipation of thermal energy and the temporal response of the resonant process place constraints on the utility of the process. Momentum conservation must be maintained and can be controlled by the interaction geometry.

There is no symmetry restriction for third-order processes, unlike the case for second-order processes, so they are exhibited by all media. In conjugated polymers, where electron oscillations are much larger in the chain direction than perpendicular to it, nonlinear responses are extremely large.

Nonresonant third-order nonlinearities are larger in polymers such as polyacetylene (Sinclair et al., 1987), polydiacetylene (Sauteret et al., 1976), and other conjugated polymers than in any other class of materials, including inorganic semiconductors. The response parallel to the chain direction suggests that macroscopic orientation of the polymer should result in a considerably larger response than in an isotropic system. The enhancement factor can be shown to be a factor of five. Conjugated liquid crystalline mainchain polymers are also known to exhibit high degrees of shear-induced uniaxial alignment, and the expected increases in nonlinear coefficients in appropriate directions have been observed (Rao et al., 1986).

All optical signal processing applications based on third-order NLO fall into two basic categories: parallel and serial. There are two approaches to parallel processing that enable the massive parallelism and interconnectivity of optics to contribute to optical computing and information processing (Gibbs, 1986). The first of these involves the use of simple spatial patterns combined with the switching behavior of nonlinear etalon devices to perform computational functions; these devices are simply miniature resonant cavities where the thickness, refractive index, and reflectivity of the internal surfaces are chosen to provide a destructive interference condition and therefore low transmission through the device. The nonlinear contribution to the refractive index of the medium, as illustrated by the equations below, causes the transmission characteristics to be light-intensity-dependent and capable of exhibiting bistable behavior.

The second approach to parallel processing involves the formation of transient holograms generated by two counter-propagating beams in a bulk nonlinear medium to alter the information content of a third beam interacting with the grating thereby producing a new fourth beam. An example of information processing by this method is associative memory (Yariv and Kwong, 1986). Here an optical mode of a resonator containing a hologram with many messages and a nonlinear medium can selectively amplify a particular message, given only partial information from an input beam. For these applications the primary requirement is for large $\chi^{(3)}$, where

$$\chi^{(3)}/\alpha = n_2 n_0 \Sigma_0 c^{2/3}$$

in MKS units and

$$n = n_0 + n_2 I$$

where n_0 is the material refractive index, n_2 is the light-intensity-dependent refractive index, and I is the light intensity and α is the absorption coefficient. A large value of n^2 maximizes the response of the material to small amounts of energy. Because of the inherent parallelism, high degrees of information throughput are generated, and response times in the nanosecond to millisecond time frame are useful.

Because of their extremely large resonant nonlinearities, GaAlAs multiple quantum wells and photorefractive crystals such as $BaTiO_3$ have a tremendous functional advantage for this class of applications. Investigations of NLO

properties of organic systems, being in a much earlier stage, have not yet demonstrated similar advantage.

Serial applications of third-order nonlinear optics involve the use of the intensity-dependent refractive index in waveguided structures to perform rapid switching of bit streams between two or more optical channels. The importance of such devices can be appreciated by realizing that optical fibers can be utilized to transmit information at rates approaching 1 THz. This rate is beyond the capabilities of known light detectors and will require all-optical signal processing before light signals are converted to electronic ones. In waveguides, long interaction lengths can be used to generate phase retardations needed for switching applications so that the premium for materials is put on the speed of the nonlinear response and the optical losses in the material caused by linear optical processes. The decay times of nonlinear responses in semiconductors and quantum well structures, as well as the response time in photorefractive materials, are in general too slow for this type of application. Polymeric materials exhibiting extremely large nonlinearities (albeit much smaller than the resonart nonlinear responses of the inorganic materials that makes them more suitable for parallel processing) may offer the best hope for this important class of applications if additional gains can be made in their properties (Stegeman et al., 1987).

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3

PROPERTIES OF LIQUID CRYSTALLINE POLYMERS:
CURRENT AND DESIRABLE CHARACTERISTICS

The properties of LCPs are dependent on their final physical forms and their modes of processing. This chapter is divided into sections dealing with structural and functional properties. These are further partitioned into subsections dealing with final forms (fibers, films, and processing), function (electro-optic), and stability of LCPs.

STRUCTURAL PROPERTIES

Fibers

Conventional fibers are prepared either by extrusion of a polymer solution into an evaporating gaseous stream (dry spinning) or into a precipitating liquid medium (wet spinning) or by extrusion of a molten polymer into a cooler gaseous environment (melt spinning). (In wet spinning of lyotropic LCP solutions, the extruded solution usually passes through an air (gas) gap before entering the coagulation bath.) The cross-section of the spin line is attenuated during the spinning process and the molecular and/or supramolecular orientation in the resulting morphological hierarchy in the filament (see Figure 2.13) is further increased by stretching (drawing) at temperatures higher than the glass transition temperature. Ultimately the molecular orientation in microfibrils composed of high molecular weight chains is responsible for the desirable unidirectional high tensile strengths and moduli of fibers. Not only is it costly to achieve high orientation via the various spinning and processing steps, but the extent of molecular orientation is severely limited by molecular entanglements and by premature crystallization resulting in a morphology wherein conventional polymer chains have a more random conformation—i.e., extensive chain folding and variably oriented chains between crystalline lamellae. Accordingly, even after annealing to extend the crystal (para crystal) component, the classical hard fibers (e.g., nylons and polyesters) exhibit tensile strengths that are limited by this basically two-phase (crystal + amorphous) morphology to values on the order of 5 to 15 gpd (equivalent to about 400 to 1400 MPa) and tensile moduli on the order of 20 to 250 gpd (about 1.5 to 22 GPa).

The LCPs, on the other hand, with their rigid, linear chains close-packed in the fluid nematic domains, orient easily in the converging flow field of the spinneret and refine their parallel orientation in the extensional flow field of the spin line, emerging in a highly oriented morphology (extended-chain crystal habit; see Figure 2.13). The orientational relaxation times are so long in the melt that solid fibers are readily formed with minimal departure of the molecular orientation from that in the fluid LC state. Annealing increases the already high orientation, resulting in exceptionally high fiber tensile strengths and moduli. For example, Du Pont's Kevlar® exhibits tensile strengths of 2.4 to 3 GPa and tensile moduli of about 65 to 145 GPa. Since Kevlar® is the most prevalent fiber derived from an LCP, an extensive tabulation of its properties is given in Table 3.1.

The temperature stability of LCPs is dramatic and may be appreciated by comparisons with ultra-high strength conventional polymers. In recent years, extremely large tensile values have been attained by "gel-spinning" of polyethylene (PE), e.g., Spectra® (Allied-Signal). However, because of the inherent molecular flexibility of PE (facile transitions among gauche and trans-isomers) and weak intermolecular dispersion forces, its melting point is low (about 145°C). Present and potentially commercial LCP fibers by contrast exhibit melting points that range from 280 to well over 400°C (decomposition). These high values are accompanied by retention of useful mechanical properties at temperatures well above those demonstrated by gel-spun PE. Table 3.2 summarizes the properties of a number of commercial and potentially commercial LCP fibers; selected Kevlar® data and those of carbon and glass are included to facilitate comparisons.

In addition to high thermal stability, LCP fibers, in common with other organic materials, have low densities relative to such inorganics as glass and metals. This translates into very favorable tensile strength-stiffness-mass characteristics (Figure 3.1), particularly significant for composites and, in turn, for use in aircraft and space applications. Note especially the very high specific strengths and specific moduli of the lyotropic rigid rod LCPs such as PBZT and PBO fiber.

The very high orientations of the LCP (and gel-spun) fibers are accompanied by poor compressive strength. To date, the only practical way to overcome this serious problem for composites has been to employ mixtures of the LCP fibers with graphite fibers. (Dow has recently reported that a developmental PBO fiber may exhibit better compressive strength (H. Ledbetter, presentation to the committee).

TABLE 3.1 Properties of Kevlar® Aramid Fibers Derived from Lyotropic LCPs

Property	Kevlar® 49	Kevlar® 149
Density	1.44g/cc (0.052 lb/in^3)	1.47g/cc (0.053 lb/in^3)
Processing	Air-gap wet spinning and heat treatment	
Yarn tensile strength*	23 gpd (2.92 GPa) 420 x 10^3 psi	18 gpd (2.29 GPa) 340 x 10^3 psi
Yarn elongation	2.5%	1.45%
Yarn initial modulus	900 gpd (124 GPa) 16.5 x 10^6 psi	1110 gpd (141 GPa) 21 x 10^6 psi
Yarn secant modulus to 1% elongation	915 gpd (116 GPa)	1230 gpd (156 GPa)
Epoxy strand tensile strength**	525 x 10^3 psi (3.62 GPa)	500 x 10^3 psi (3.45 GPa)
Epoxy strand elongation	2.9%	1.9%
Epoxy strand modulus	18-19 x 10^6 psi (124-131 GPa)	25-26 x 10^6 psi (172-179 GPa)
Refractive index—		
‖ Fiber axis	2.0	
⊥ Fiber axis	1.6	
Equilibrium moisture regain (25°C, 65% R.H.)	4.3%	1-1.5%
Yarn creep rate/log time change	0.020% (load 41% ultimate T. Str.)	0.011% (load 58% ultimate T. Str.)
Fiber coefficient of thermal expansion (longitudinal) m/m/°C	-4.25 x 10^{-6}	-1.96 x 10^{-6}

TABLE 3.1   Properties of Kevlar® Aramid Fibers Derived from Lyotropic LCPs
            (continued)

Property	Kevlar® 49	Kevlar® 149
Dielectric constant, K (Fabric/Fiberite® 934 Epoxy Laminate)	4.14 at 10^6 Hz	3.90 at 10^6 Hz
Electron radiation (0-200 megarads)	100% of strength & modulus retained	
Shrinkage (permanent)	< 0.09% after 250°C exposure	
Flammability	Self-extinguishing	
Limiting oxygen index	29	
Thermal decomposition temperature (TGA)	500°C (930°F)	
Long-term use temperature in air	160°C (320°F)	
Tensile properties at 180°C (355°F)	> 80% of room temp. strength & modulus retained	> 90% of modulus retained
Chemical resistance, bare yarns	Resistant to most solvents and chemicals but can be degraded by strong acids, bases, and steam	More chemically resistant than Kevlar® 49
Ultraviolet stability	Degrades, but degree depends on material thickness since Kevlar® aramid is a strong absorber and is self-screening. In composites, strength loss not observed.	

TABLE 3.1 Properties of Kevlar® Aramid Fibers Derived from Lyotropic LCPs
(continued)

Property	Kevlar® 49	Kevlar® 149
Production plant capacity:	Kevlar® in general:	
Richmond, Virginia	45 million lb/yr	
Maydown, Ireland	15 million lb/yr	

*Yarn properties determined on 10" twisted yarns (ASTM-D885).
**Strand properties determined on untwisted epoxy impregnated yarn (ASTM-D2343).

Source:

- Chem. and Eng. News, July 11, 1988, p. 15.

- Du Pont Data Manual for Kevlar® 49 Aramid, May 1986.

- Du Pont Publication E-95612, 6/87, Kevlar® 149, Properties and Characteristics of Yarn and Composites.

- Riewald, P. G. 1988. Advanced Textile Materials Conference, Clemson University, Greenville, S.C., April 5-6.

- Riewald, P. G., A. K. Dhingra, and T. S. Chern. 1987. ICCM and ECCM, Sixth International and Second European Conference on Composite Materials, July 20-24, 1987, Vol. 5, pp. 5362-5370, F. L. Matthews, N. C. R. Buskell, J. M. Hodgkinson, and J. Morton, eds. New York: Elsevier Applied Science.

TABLE 3.2 Yarn Properties of Some Reinforcing Fibers From LCPs

Property		Kevlar® Aramid			Twaron® Aramid 1-1000	H.T.* PBZT	Vectran® HS	Ekonol®	Carbon/Graphite		Glass S-2
		29	49	149					Hi T	Hi Mod	
Tensile strength	gpd**	23	23	18	22	25-30	20-25	30	23	11	16
	Kpsi	425	425	340	406	506-607	360-450	538	521	249	510
	MPa	2930	2930	2345	2797	3488-4185	2472-3090	3708	3595	1904	3518
Elongation	%	3.6	2.5	1.45	3.3	1.0-1.4	2.2-2.5	2.4	1.5	0.4	4
Initial modulus	gpd	525	900	1110	630	2100-2400	680-840	1100	1500	3000	400
	Mpsi	9.7	16.6	20.5	11.6	42.5-48.5	12.2-15.0	19.7	34.0	75.3	12.7
	GPa	67	114	141	80	293-335	84-104	140	234	519	88
Secant modulus to 1% elongation	gpd		915	1230	630						
	Mpsi		16.9	22.7	11.6						
	GPa		116	156	80						
Denier		1140	1140	1140			1500-200				
Density	g/cc	1.44	1.44	1.47	1.44	1.58	1.40	1.40	1.77	1.96	2.49
Moisture regain	25°C, 65% RH %	4.3	4.3	1.0-1.5	7		<0.1				
Creep rate vs. log time; load-40-58% ultimate T. Str.	%	0.052	0.020	0.011			0 (77 days, loaded at 33% breaking strength)				
Melting point	°C	None	None	None	None	None	327-331				
Shrinkage	%		<0.09 (after 250°C exposure)				<0.5 (boiling H_2O), <0.5 (350°F air)				
Coefficient of thermal expansion (logitudinal)	in/in/°F	-4.25×10^{-6}		-1.96×10^{-6}			-2.7×10^{-6}				
	m/m/°C						-4.8×10^{-6}				

TABLE 3.2 continued

*Heat treated PBZT—Tensile properties determined on <u>filaments</u>, one-inch length for tenacity, ten-inch for modulus.

**gpd = grams per denier—a specific strength or modulus determined by dividing yarn break strength in grams by denier. Denier = weight/length in units of grams per 9000 meters.

Source:

- Du Pont Publication E-95612-6/87, Kevlar® 149, Properties and Characteristics of Yarn and Composites.

- Hoechst Celanese Publication, Hoechst Celanese Vectran® HS Fiber, February 1, 1988.

- Riewald, P. G. 1988. Advanced Textile Materials Conference, Clemson University, Greenville, S.C., April 5-6.

- Riewald, P. G., A. K. Dhingra, and T. S. Chern. 1987. ICCM and ECCM, Sixth International and Second European Conference on Composite Materials, July 20-24, 1987, Vol. 5, pp. 5362-5370. F. L. Matthews, N. C. R. Buskell, J. M. Hodgkinson, and J. Morton, eds. New York: Elsevier Applied Science.

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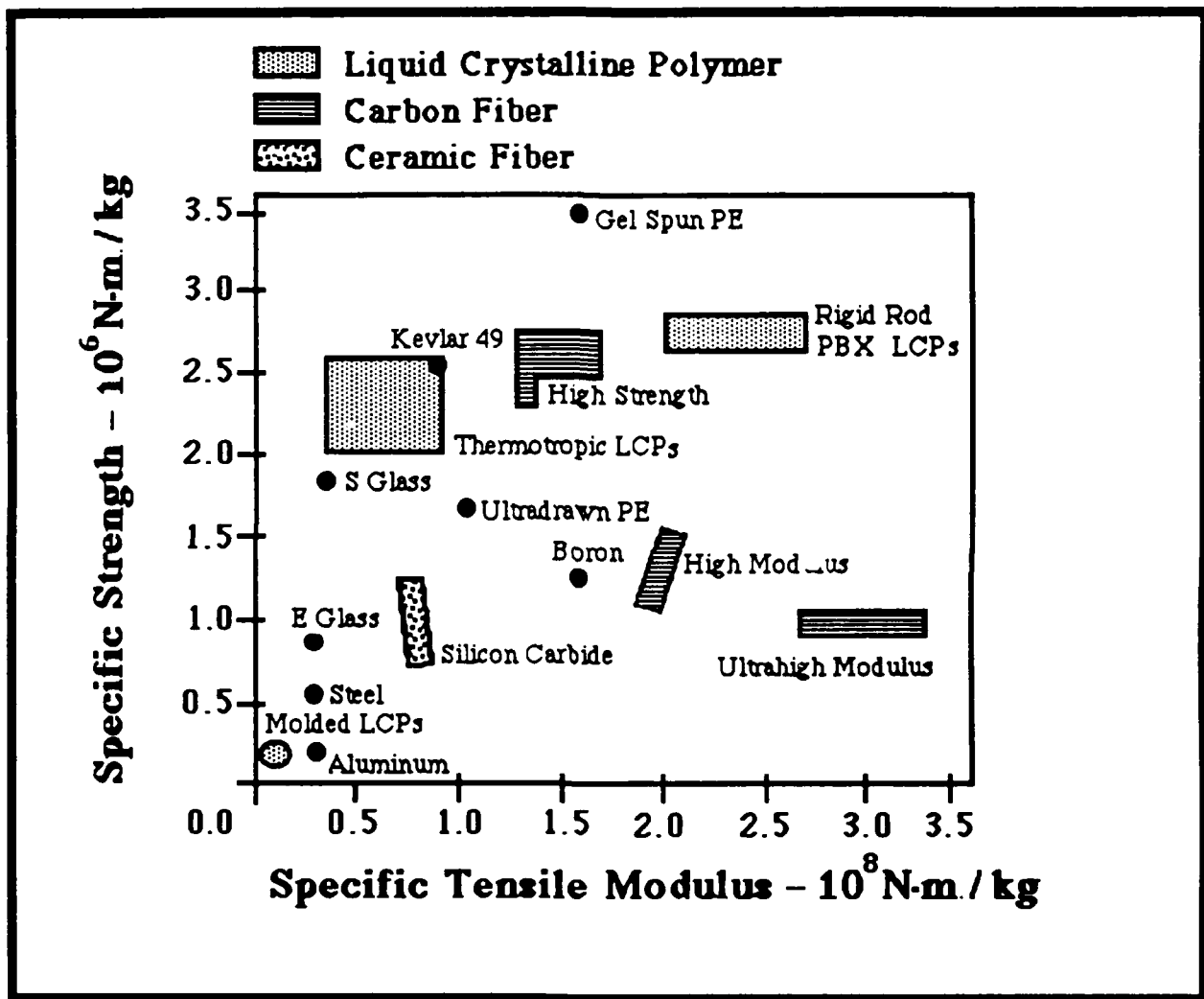
FIGURE 3.1 Specific tensile strength versus specific tensile modulus showing
LCPs in context with other materials.

Injection Molding

The properties of injection molded bars of commercially available melt-processible LCPs as reported in the trade literature are given in Table 3.3. ICI's Victrex® SRP-1 is believed to be a copolymer of hydroquinone (HQ), isophthalic acid (IA), and p-hydroxybenzoic acid (HBA). Hoechst-Celanese's Vectra® A series is a copolymer of HBA and 6-hydroxy-2-naphthoic acid (HNA) (approximately 73/27 HBA/HNA); Victrex® SRP-2 is believed to be similar. Amoco Performance Plastic's Xydar® SRT-300 is a terpolymer of HBA, 4-4'-biphenol (BP), and terephthalic acid (TA). Xydar® G-330 and Sumitomo's Ekonol® 6000 are similar and probably also contain small amounts of IA; the former is glass filled. Other melt-processible polymers have been announced by Du Pont and Granmont (Montedison); the latter is commercializing technology acquired from Owens-Corning Fiberglas Corporation. The Eastman Chemicals copolymer based on PET and HBA, originally introduced as X7G, is also available commercially in Japan. Other commercial announcements in Europe and Japan are expected.

The various LCPs differ primarily in their high-temperature characteristics. Therefore, a tabulation on the basis of temperature is useful (Table 3.4). Xydar® test pieces (based on SRT-300) demonstrate heat distortion temperatures under load (264 psi) in the 300 to 355°C range. An Underwriters' Laboratory rating of 240°F for continuous electrical service is reported, with excursions to over 600°F permitted. The polymer exhibits melting points of 390 to 420°C and demonstrates excellent oxidative thermal stability at high temperatures. LCPs useful in such high temperature ranges are known as Type III LCPs.

Type II LCPs demonstrate melting points some 100 to 150°C lower than Type III LCPs. This translates into lower use-temperature ranges. The Vectra® and Victrex® SRP polymers fall into this category. Because of the lower melting points, the Type II LCPs are processible at lower temperatures. This is appealing for manufacturing molded parts that do not require the very-high-temperature properties associated with type III.

Type I LCP properties are dominated by low glass transition temperatures and little or no crystallinity, and they demonstrate much lower use temperatures as a result. The X7G is such a polymer.

All commercial melt-processible LCPs demonstrate a number of common characteristics. Tensile and flexural moduli of unfilled injection-molded test bars, at room temperature, are in the 1 to 3 Mpsi range. Such moduli are characteristic of glass-filled semicrystalline polymers; hence, these LCPs are often described as "self-reinforced" polymers. These high moduli decrease as the temperature is raised; the higher the melting point of the polymer, the greater is the temperature range over which properties remain useful.

TABLE 3.3 Properties of Injection-Molded ASTM Bars

Name	Unfilled Polymers					30% Glass-Filled Polymers				
	Victrex® SRP-1	Victrex® SRP-2	Vectra® A-900	Xydar® SRT-300	Ekonol® 6000	SRP-1 1500GL30	SRP-2 2300GL30	Vectra® A-130	Xydar® RC-210	Xydar® G-330
Density (g/cm^3)	1.38	1.38	1.4	1.35	1.40	1.56	1.56	1.57	1.60	1.62
Tensile modulus (Mpsi)			1.4	2.0	1.1			1.5	2.3	1.7
Tensile strength (Kpsi)	33	31	24	16		25	29	29	20	17
Flex modulus (Mpsi)	1.9	1.6	1.3	2.0	2.0	2.3	2.2	2.1	1.9	1.8
Flex strength (Kpsi)	25	28	25	20	22	40	38	36	23	23
DMA modulus (Mpsi) at 25°C	1.7	1.7		1.9		1.9	2.2	2.4	2.6	
50	1.6	1.4		1.7		1.8	1.9	2.3		
100	1.3	0.6		1.4		1.6	1.0	1.7		
150	0.25	0.4		1.2		0.45	0.75	1.1		
200	0.2	0.3		1.1		0.35	0.60	1.1		
250	0.15	0.05		1.0		0.3	0.10	0.8	1.4	
300	0.0	0.00		0.8				0.4		
350				0.6				0.0		
Melting point (°C)			280	420	321					
Heat distortion temp. at 264 psi (°C)	170	190	180	355	250	231	231	229	346	266
Coefficient of linear thermal expansion ppm/°F (flow direction)	6	6	6	0	6	8	0		6	
(transverse)	42	42	63		60	15	19			
H$_2$O absorption (equilibrium %)	0.2	0.16	0.02			0.13	0.14		<0.1	<0.1
Limiting oxygen index (%)	39	36	36	42		38	38	37	46	
Dielectric strength (v/mil)	>560	>640		6(.		560	>610		640	

TABLE 3.4 Classification of LCPs According to Thermal Behavior

Polymer	Type	Limited by
Xydar® (SRT-300)	III	T_m = 420°C
Vectra®	II	T_m = 280°C
X7G	I	T_g = 80-100°C

Both moduli and breaking strengths (10,000 to 40,000 psi) of bars depend on the gauge of the test specimen as well as the LCP type. This gauge effect arises from a marked skin-core morphology, with more flow-direction orientation located in the skin. Accordingly, the thinner the part, the greater the strength and modulus; the effect is illustrated for Xydar® in Table 3.5.

TABLE 3.5 Effect of Gauge on Flexural Strength and Modulus (ASTM Test Bars)

Gauge (inches)	Xydar® SRT-300 (Unfilled)		Xydar® (50% Mineral)	
	Strength (10^3 psi)	Modulus (10^6 psi)	Strength (10^3 psi)	Modulus (10^6 psi)
0.125	19.7	1.81	15.3	1.57
0.0625	23.8	1.98	17.1	1.78
0.0313	29.6	3.11	18.0	1.80

Source: Duska, J. 1986. Plastics Engineering (December).

The combination of fountain flow (affecting the skin), complex flow in the core, and long relaxation times results in properties that can be very different in the flow and cross-flow directions. Anisotropy is, of course, responsible for the desirable strength and stiffness of fibers. In molded parts, however, it is usually undesirable. Both this anisotropy and the skin-core effects might be considerably mitigated by proper choice and level of fillers, resulting in more evenly distributed physical properties. However, the choice and compounding of fillers into the various polymers is more an art than a science.

The LCP domain structure also results in very low viscosities and substantial shear-thinning. This viscosity behavior is basically what distinguishes these materials from other filled high-performance polymers. Thus, although some fiber reinforced non-LCP aromatic polymers may match many of the physical properties of LCPs, the latter are preferred for filling long, thin mold sections. Such low viscosities also permit heavy filler loadings. This not only helps to smooth out the uneven directional properties referred to above, but it can also lower the cost of the relatively expensive base polymers. Indeed, thermotropic LCP manufacturers do not recommend neat polymers (except for extrusion) but, rather prefer to develop compounded resins containing minerals—e.g., talc, glass fibers, and carbon fibers. It should be noted that LCP viscosities are sensitive to thermal and shear histories. It has been reported that processing temperatures can sometimes be reduced by first raising, then lowering the temperature to the processing temperature. Similarly, "pre-shearing" may lower the viscosity.

The all-aromatic structures of Xydar® and Vectra® (and presumable Victrex® SRP) translates into high resistance to burning. A particularly dramatic demonstration involved playing an intense 2000°F torch on a plaque of Xydar® without burn-through and with minimum transfer of heat, under conditions that cut through a similar size aluminum panel. Such behavior, coupled with very low smoke generation, points to utility in military and commercial aircraft.

One should not overlook the excellent resistance of these polymers to most solvents. As with all polyesters, they are subject to hydrolysis, but only under severe conditions. This much greater resistance to hydrolysis, relative to such conventional polyesters as PET, is also a consequence of the rigid nature of the LCP molecular structures and the accompanying highly oriented, dense skin. (This is related, no doubt, to the reported excellent vapor barrier properties discussed below.) It appears that the higher the melting point of the LCP base polymer, the greater is the resistance to solvents and chemical attack. For example, Xydar® SRT-300 is not affected by pentafluorophenol, whereas Vectra® will dissolve or swell markedly.

Another important consequence of the high degree of molecular alignment is a very low linear coefficient of thermal expansion in the direction of flow with values approaching those of ceramics. Related to this are very low shrinkages on molding. Proper choice and levels of fillers even out properties and minimize warpage. The low viscosities, coupled with the low shrinkages and in-plane coefficients of expansion, allow for the molding of dimensionally stable, high-precision parts.

High dielectric strengths make for excellent insulating properties. High-temperature resistance is required to stand up to the demands of wave and vapor-phase soldering, IR reflow, and burn-in testing. These are characteristic of aromatic LCPs, and consequently these polymers (usually with fillers) are prime candidates for electrical and electronic applications, including electronic and optical connectors, chip carriers and sockets for integrated circuit mounting and testing. The continuing advances in miniaturization and automation in assembling electronic arrays will require new materials, and all indications are that there will be increased use of LCPs in these future applications.

Finally, one area that is a significant problem in injection molding of LCPs is that of poor weld strength. When two polymer flow fronts meet, the strength of the resulting joint is lower than that of the bulk. This results from poor molecular interpenetration and incomplete entanglement of the molecules. In the case of the LCPs, because of the rigidity of the molecules, the decrease in strength is particularly severe. Of the various stratagems employed to compensate for this defect, the most promising approaches involve optimizing mold and gate designs.

In summary, the LCP manufacturers encourage the use of their resins in electrical and electronic, aviation and other transportation, chemical processing, fiber optics, and aerospace applications. Starting from a low volume base, LCP consumption has been predicted to grow at least 15 to 20 percent a year, far outpacing the growth rate of conventional engineering resins.

Extrusion

Extrusion as a mode of processing LCPs to produce film and sheet has not been exploited to any great extent because of difficulties in producing uniform gauges and properties in practical widths. Markedly unbalanced properties, i.e., weak transverse properties relative to the machine direction result from the high orientation in the flow direction. The characteristically low elongation of LCP melts makes it difficult to draw biaxial films or to blow films to the ratios required for useful balanced properties. Nonetheless, a few extrusion-grade LCPs are offered, primarily among the Type II thermotropic polymers and recently films and sheets of Vectra® have been introduced. PBZT films from lyotropic dopes with tensile strengths and moduli of 80 to 100 Kpsi (0.55 to 0.69 GPa) and 30 Mpsi (207 GPa), respectively, have been reported (R. Lusignea, presentation to the committee).

There is significant motivation for the development of LCP in sheet form for thermoforming. The excellent resistance to burning, when coupled with light weight and high stiffness, make LCPs potentially very attractive for use in aircraft. Another incentive for developing LCP films lies in the increasingly attractive barrier properties that are being uncovered. Table 3.6 lists some values for LCPs versus more conventional polymers.

TABLE 3.6 Comparison of Barrier Properties of LCPs and Other Polymer Films

Material	Temp., °F.	Oxygen permeability, cc-mil/100 in²-day-atm.			Moisture vapor transmission, g.-mil/100 in²-day		
		0% R.H.	75% R.H.	100% R.H.	75% R.H.	90% R.H.	100% R.H.
Vectra A900							
0.75 mil	73	0.08	-	0.05	-	-	0.07
	100	0.35	-	0.15	-	-	0.13
7 mils	73	-	-	-	-	-	-
	100	0.20	-	0.20	-	-	0.03
EVAL-F	77	0.012	-	1.2	-	-	-
	104	-	-	-	-	3.8	-
EVAL-E	77	0.12	-	0.77	-	-	-
	104	-	-	-	-	1.4	-
Saran (extruded)	73	-	0.15	-	-	-	-
Dow XU-32009.00	100	-	-	-	0.1	-	-
Polypropylene	73	-	5-9	-	-	-	-
	100	-	-	-	0.25-0.07	-	-

Source: McChesney, C. E. and T. R. Dole. 1988. *Modern Plastics* (January).

FUNCTIONAL PROPERTIES

Desirable Electro-Optical Properties

There are several categories of second- and third-order nonlinear optical (NLO) processes that must be considered to delineate desired properties and compare the potential advantages (or disadvantages) of LCPs relative to alternative polymeric or inorganic materials. In some cases a clear advantage is perceived for the organic and polymeric materials, whereas, for others, various classes of inorganic materials either suffice or are superior. In general, liquid crystallinity provides anistropy in the medium that can lead to larger nonlinear coefficients.

Table 3.7 lists general goals that are perceived to be important for electro-optical applications (Stegeman and Lytel, 1989). For some applications active stabilization and feedback might be used where properties fall short of requirements.

TABLE 3.7   Important Requirements for NLO Applications

- $<0.1\%$ drift in $\chi^{(2)}$ and n for 5 to 10 years

- Electro-optic coefficient equal to or greater than $LiNbO_3$

- Sufficient optical clarity for 0.1 to 0.5 db/cm attenuation at 0.85 μm, 1.3 μm, and 1.55 μm

- Low dispersion in the optical and microwave regions

- $<0.1\%$ variation in thickness

- High thermal conductivity

For second-harmonic-generation applications, some additional requirements are needed; these are listed in Table 3.8 (Stegeman and Lytel, 1989).

These requirements should be viewed as general and will vary for specific applications. They are biased toward thin-film optical devices as opposed to bulk devices, for which many single-crystalline materials exist. For serial processing of information, a premium is put on turn-off time (τ) of the nonlinear response for high throughput, low absorption coefficient for low

TABLE 3.8 Requirements for SHG Applications

- Low refractive index dispersion between ω and 2ω

- $\chi^{(2)} > 10^{-7}$ esu/cm^4

- No 2-photon absorption

- Low optical absorption at fundamental and harmonic frequencies

- Photochemical stability

---

attenuation and thermal stability, and high nonlinear coefficient. A list of requirements that would permit development of all-optical serial switching devices is given in Table 3.9 (Stegeman and Lytel, 1989).

TABLE 3.9 Requirements for Optical Serial Switching Devices

- $n^2 > 10^{-14}$ M^2/W

- High device throughput $\alpha L < 0.2$ for 80% throughput (α is adsorption and scattering losses and L is interaction length) at 1.55 μm and α approximately 0.1

- Low-temperature dependence of n and n^2

- $\pm$ 100 Å dimensional stability

- Processible into waveguides

- High damage threshold > 10 GW/cm^2

- n^2 relaxation time < 10^{-12} sec

- Figure of merit $W = \Delta n_{sat}/\alpha\lambda$ approximately 0.5 to 2.0 (device dependent), where Δn_{sat} is the saturation value of the nonlinear refractive index, α is the absorption coefficient, and λ is the wavelength

---

Currently Available Electro-Optical Properties

The predominantly used electro-optical material for integrated optics applications is $LiNbO_3$. It has excellent electro-optical properties and can be fabricated into high-quality waveguided devices with both active and passive components for modulation, switching, and information-processing applications. Methods for manufacturing, device engineering, and fabrication are mature. Excellent progress has been made in device packaging and in hybrid technologies for electrically driving the devices. Another relatively new NLO material that is both more efficient than $LiNbO_3$ and is free from many of its deficiencies is potassium titanyl phosphate (KTP) (Bierlein and Vanherzeele, 1989).

In spite of many years of effort, however, $LiNbO_3$-based integrated optic technology has not become widespread and pervasive. There are several reasons for this. First is the cost of manufacturing high-quality, impurity-free substrates for processing into devices. Although device-grade material is readily available today, impurity-controlled optical damage was a problem for many years. Second, the predominant waveguide formation technology involves high-temperature diffusion of titanium into $LiNbO_3$, and minor differences in one of a number of processing parameters can have a major impact on device performance. Third, $LiNbO_3$ is not readily integrated with silicon- or GaAs-based technology. Because of the predominance of silicon in the electronics industry and the promise of III-V compound semiconductors for performing both optical and electronic functions, considerable attention may be shifting toward these technologies in the future. Even though KTP appears to be an excellent NLO and electro-optical material it will continue to be incompatible with silicon or GaAs unless progress is made in growing thin films of the material.

It is noteworthy that, with relatively modest research efforts, poled polymeric materials have been shown to exhibit electro-optic coefficients similar to $LiNbO_3$ with low losses of approximately 0.8 db/cm at 0.83 μm. Polymers have a tremendous potential advantage relative to $LiNbO_3$ in that they can be spin-coated or cast, which significantly increases their chances of being compatible with integration on silicon and GaAs substrates. Preliminary demonstrations of waveguide formation by poling with patterned electrodes look promising for some types of devices, and GHz responses have been measured in traveling-wave devices (Carney and Hutcheson, 1987). Reports of gradual deterioration of induced alignment have been a major source of concern for poled polymers (Ye et al., 1988), as is transparency in the important 1.3 μm and 1.55 μm regions because of -C-H vibrational overtones.

For second-harmonic-generation applications, the situation with respect to materials is much more complex. The major drive for this technology, aside from spectroscopic applications, is the conversion of 825-nm output of laser diodes to 412 nm for optical memory applications. Proton-diffused $LiNbO_3$ waveguides have been shown to convert significant amounts of 1060-nm light to 533 nm, but with very poor beam quality (see New Scientist, 1988). A variety of intracavity second-harmonic-generation and frequency mixing devices have been demonstrated with miniature KTP crystals in conjunction with diode laser-pumped miniature Nd:YAG rods, and these are now commercially available.

Because of the superior properties of KTP, including a large $\chi^{(2)}$ of 3 x 10^{-8} esu, excellent transparency, and linear optical properties, this material shows great promise for frequency doubling and mixing applications. However, the low nonlinear coefficient requires high-power diode lasers (Risk et al., 1988).

Very little has been reported in the literature to date on poled polymers designed for harmonic generation to 412 nm. A major problem is the trade-off between transparency of a nonlinear chromophore in the visible region of the spectrum and the magnitude of its nonlinear coefficient. A second problem is the nature of the $\chi^{(2)}$ tensor for materials with electric field polar symmetry, which makes phase matching (matching the phase velocity of fundamental and harmonic waves) difficult in bulk devices. Sophisticated waveguide structures using polymers might permit this. The main reasons for considering polymeric materials for this class of applications are the potential for high nonlinear coefficients, possibly an order of magnitude larger than KTP, and the potential for integration with diode laser light sources.

In discussing material properties for third-order nonlinear effects, it is convenient to follow the distinction made earlier between those used in devices for parallel processing and serial processing.

In parallel processing, two-dimensional arrays of pixel-like elements are likely to be switched between on and off states in response to input and control optical signals. Various devices have been proposed and investigated for this purpose, ranging from nonlinear Fabry-Perot cavities that act as bistable devices to thin-film semiconductor heterostructure devices made of multiple quantum well (MQW) material. One example of the latter is a self-electro-optic device (SEED) that acts as a light-triggered switch (Miller et al., 1984). Because throughput through such devices is highly parallel, they are capable of handling large amounts of information. A premium is put on optical power requirements in such devices, as opposed to the switching rate of the device. In serial processing, bandwidth is determined by the number of switching operations per second. All optical devices with subpicosecond response times have a clear advantage relative to electronic devices, whose response times are several orders of magnitude longer for this type of application (Stegeman and Lytel, 1989).

The light-intensity-dependent refractive index n^2, response time r, absorption coefficient α, saturation value of the refractive index Δn_{sat}, and FOM $W = \Delta n_{sat}/\alpha\lambda$ for a variety of materials are shown in Table 3.10 (Stegeman et al., 1987). Where NR appears in the table, the measurement was made under nominally nonresonant conditions. This does not imply, however, that α is negligible. Values of Δn_{sat} were not reported for a number of the polymers, but if one assumes they are similar to those for PTS away from and near resonance, several observations can be made. First, n^2 for GaAlAs MQW devices on resonance is extremely large relative to PTS on resonance. The power per bit to switch a bistable device is 6 to 7 orders of magnitude less for the MQW than for the polymer. Since the switching rate is adequate for highly parallel computational architectures, it is clear that organic systems of the

TABLE 3.10 NLO Materials Properties (Inorganic and Organic)

Waveguide Material	n_2, M^2/W	τ, sec	α, cm^{-1}	Δn_{sat}	W
MQW-GaAlAs					
On resonance	$\sim 10^{-8}$	10^{-8}	10^4	0.1	0.1
Off resonance	$\sim 10^{-12}$	10^{-8}	30	$\sim 2 \times 10^{-3}$	~ 0.9
CdSSe-doped glass	$\sim 10^{-14}$	10^{-11}	~ 3	5×10^{-5}	~ 0.3
PTS					
On resonance	2×10^{-15}	$\sim 2 \times 10^{-12}$	10^4	~ 0.1	~ 0.2
Off resonance	10^{-16}	$<0.03 \times 10^{-12}$	10^2	$>10^{-3}$	>0.15
Poly-4-BCMU	6.4×10^{-16}	$<10^{-13}$	NR		
PBZT	10^{-17}	$<10^{-13}$	NR		
Polythiophene	8.5×10^{-16}	$<10^{-12}$	6×10^3		
Phthalocyanine	6.4×10^{-15}	$<10^{-12}$	6.9×10^4		
SiO_2 glass	10^{-20}	$<10^{-13}$	10^{-5}	$>10^{-7}$	>20
SiO_2, Pb-doped	10^{-18}	-	-	-	-

PTS type cannot compete for these applications. On the other hand, the dimensionless quantity W discounts the power requirement for a switching operation and emphasizes throughput—i.e., the amount of refractive index change that can be achieved relative to the amount of light dissipated in the material. It is independent of the power and length of interaction required for switching. This parameter is much more applicable to the operation of waveguided devices likely to be used in serial switching operations.

It is noteworthy that PTS is close in value to the MQW structures. Its response time is many orders of magnitude shorter, making it much more suitable for high-speed applications. The value of W = 20 for glass is impressive but misleading, since it reflects the extremely low α of glass. Extremely long path lengths and high powers would be required to operate devices made from this material. The large nonresonant n_2, combined with

polymers for all optical serial switching operations. The second requirement for the class of devices listed in Table 3.9 is critical for device operation and will be extremely difficult to achieve in polymeric materials. A trade-off exists between this requirement and the magnitude of n^2 as long as α is sufficiently small, i.e., less than 0.1. A gain of two orders of magnitude in nonresonant n^2 would result in a shorter interaction length and smaller switching power and would ease the constraints on device design and motivate considerable device-related research on such materials.

ENVIRONMENTAL STABILITY

The environmental stability and durability of LCP-derived structures, devices, and products is a broad and complex subject, especially when certain factors unique to military materiel are considered. These environmental factors fall into two major categories: those associated with the natural environment and those imposed by the end use or application environment. In the former category, temperature and moisture are the most significant, with UV radiation and environmental pollutants such as the oxides of sulfur and nitrogen sometimes playing a role. In the latter, temperature may be a consideration, but application-specific factors such as operational fluids, including fuels, lubricants, and de-icers, must also be considered. Of special concern to the military is the need to withstand the effects of chemical warfare (CW) liquids for both short- and long-term exposures.

The nature of the application will dictate the degree to which environmental exposure is experienced. For example, consider an LCP-based component in an optical computer operating in an air-conditioned, temperature-controlled communications center, as contrasted with a Kevlar® aramid-based composite aircraft structural element exposed to an entire spectrum of environments: from the tropics to the arctic, from ground level to 40,000 feet, etc. The standards for durability are clearly different for these two cases.

The chemical and physical nature of the polymer will also affect response to environmental exposure. Polymers that contain hydrolytically susceptible linkages, such as polyesters and polyamides, are at greater risk in hot and wet conditions, particularly in the presence of catalytic species such as acids or bases, than are hydrocarbon or fluorocarbon polymers. Similarly, amorphous polymers are usually more prone to hydrolysis than are semicrystalline or crystalline materials because of the reduced diffusion of water in the latter.

Resistance to CW liquids can be viewed as a specialized aspect of durability peculiar to military materiel. Those liquids fall into two categories: chemical agents and decontaminants. For the toxic agents, the major concern is that a material may absorb a quantity of the agent and, through diffusion, rerelease it at a time and place such as a maintenance facility where its presence is not anticipated. The consequences for un-protected personnel could be catastrophic.

In the case of decontaminants, the issue is the degradation of physical and mechanical properties, both short- and long-term. This is especially true for the most common decontaminant, DS-2, an extremely caustic mixture of sodium hydroxide, diethylenetriamine, and methyl cellosolve. This aggressive fluid has already been shown to attack a variety of organic materials. For instance, immersion in DS-2 leads to the complete dissolution of polycarbonate (Lee and Vanselow, 1987), while a glass/polyester composite gained over 6 percent in weight during extended exposure (Wentworth, 1986). In light of this, it seems likely that certain classes of LCPs, most notably the thermotropic polyesters and the aramids, will be adversely affected by exposure to CW liquids.

Although environmental exposure, whether natural or applications-related, can lead to deterioration of LCP-derived articles and structures, this fact should not be regarded as an indication that LCPs are unsuitable. It is clear, however, that during the materials selection process careful consideration must be given to the range of environments to which the item will be exposed and that the material must be evaluated for its response to that range of environments. In some cases, such data may already exist in the literature. The environmental response of Kevlar® aramid, for example, is well documented (Morgan and Allred, in press). Where appropriate, this includes an assessment of the effect of CW liquids. Even in those cases where an unacceptable effect is observed, it is likely that adequate protection, probably in the form of coatings, can be provided to reduce the effect to acceptable levels. Indeed, there are reports that the thermotropic polyesters themselves exhibit exceptional barrier properties (Chiou and Paul, 1987) and may be viable candidates as protective coatings in their own right.

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4

PROBLEMS AND ISSUES: RECOMMENDATIONS FOR FURTHER WORK

MACROMOLECULAR DESIGN AND SYNTHESIS

Sidechain LCPs

Although not suited for structural use, sidechain LCPs have potential as functional materials. The anisotropic organization of pendant groups can be intimately related to function, as, for example, in the nonphotobleachable colored film materials derived from cholesteric sidechain polymers (Shannon, 1984). In this case and in general, mesomorphic structure is readily frozen into a glassy mesophase without crystallization as the polymer is cooled below its glass transition temperature (T_g).

Retention of mesophase positional alignment and dipolar orientation upon electric field poling while cooling below T_g can lead to bulk noncentro- symmetry in a mesomorphic system (Meredith et al., 1982). Development of properties dependent on an acentric structure, such as certain NLO effects, piezoelectricity, and pyroelectricity, is possible if the structural chemistry of the polymer is designed properly. To the degree an anisotropic arrangement of functional species can contribute to enhancement of these effects, a mesogenic polymer is advantageous.

Ferroelectric behavior has been observed for smectic C sidechain LCPs (Shibaev et al., 1984). Electro-optical devices based on ferroelectric LCs are known (Clark and Lagerwall, 1984). Although usually slower in response than low-molar-mass ferroelectric LCs, advantage can be taken of their polymeric nature. Since surface-stabilized ferroelectric LCs are in a sense "self-poling," a combination of ferroelectric and, for example, NLO properties in a single material would be attractive.

Lightly cross-linked LCPs, to date primarily sidechain LCPs, can be elastomeric above T_g (Finkelmann et al., 1981). These elastomers exhibit orientation of mesogenic pendant groups upon application of stress to the network. LCP elastomers have been envisioned as optical waveguides and as

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selective barrier materials (membranes). In situ photopolymerization of sidechain LCPs in the mesophase has been recently demonstrated and is perceived (Broer et al., 1988; Hoyle et al., 1988) as a processing option that may lead to high-speed formation of LCP films and coatings. In addition, masking techniques used with in situ photopolymerization are seen as potentially useful for integrated optics, displays, and optical information discs. Laser-addressed smectic sidechain LCPs have been described for information-storage applications (Hopwood and Coles, 1985).

Historically, the synthesis of sidechain LCPs has been primarily free-radical vinyl polymerization of acrylate or methacrylate monomers. Recently, combined sidechain and mainchain LCPs have been described (Reck and Ringsdorf, 1985) based on a polyester mainchain. There has been rapid development of synthetic methodology toward introduction of new mainchains for sidechain LCPs including polysulfones (Braun et al., 1987), polyesters (Griffin et al., 1988), and polyurethanes (Tanaka and Nakaya, 1988). Polysiloxanes (Finkelmann and Rehage, 1980) and, more recently, polyphosphazenes (Singler et al., 1987) have been used for reactions in which a mesogenic pendant group is grafted onto the polymer backbone. Sidechain LCPs from these preformed polymers and from new polymer backbones offer interesting auxiliary properties, such as variability in T_g, solubility, stability, etc. Hence, it is recommended that attention be paid to novel functional sidechain (and mainchain) LCPs. Opportunities for exploiting the interplay of function and chemical structure in these anisotropic systems should be taken where their structural anisotropy and glassy mesophase formation can lead to enhanced performance.

Thermotropic LCPs

Among the serious structural issues arising in LCP polyester syntheses are the elucidation and control of the mer sequence along the polymer backbones (Economy et al., 1989; Mühlebach et al., 1988). At best, one can only see dyads via high-resolution NMR in the solid state or in solution (where soluble). These tend to confirm X-ray studies, which conclude that the sequences are essentially random (in other than the trivial simple A-A B-B case) (Blackwell and Biswas, 1986). Given the heterogeneous nature of polymerizations involving free terephthalic acid as well as differences in condensation rates, blocky sequences would be anticipated in the absence of extensive transesterification. Clearly, the latter is an important accompanying reaction as confirmed recently (Economy et al., 1989; Jin 1989); controlled sequence distributions were shown to randomize rapidly by interesterification on heating. To control the sequence distribution, new polymerization techniques and/or catalysts and transesterification inhibitors will have to be developed, as well as improved methods to measure the resulting distributions. Until these are accomplished, the structure-property relationships associated with backbone sequence and subsequent design of possibly improved polymers will be severely hampered.

Monomer Costs

The reason for the commercial and military importance of LCPs resides in their unique properties. However, their commercial future and availability is intimately tied to lowering their cost. In turn, this is largely determined by the cost of the monomers required for their manufacture. The LCPs that are most significant from a commercial and/or military viewpoint are derived essentially from all-aromatic monomers.

The significant monomers for commercial and near-commercial thermotropic polyesters include A-B as well as A-A and B-B types. The latter include the diols, such as 4,4'-biphenol (in Amoco's Xydar® and Sumitomo's Ekonol®), hydroquinone (in ICI's SRP) and phenylhydroquinone (Du Pont), and the diacids, including terephthalic and isophthalic acids. The significant A-B monomers are 4-hydroxybenzoic (in most LCPs) and 6-hydroxy-2-naphthoic acids (in Hoechst-Celanese's Vectra®). Of the above, the lowest-cost monomers are the diacids, at substantially less than $1.00/lb. Next in price are hydroquinone (potentially) and p-hydroxybenzoic acid, at less than $2.00/lb. The most expensive of the thermotropic LCP monomers are 4,4'-biphenol and 6-hydroxy-2-naphthoic acid, at somewhere between $3.00/lb and $10.00/lb. Phenylhydroquinone is probably included in the latter range.

Of the lyotropic LCP monomers, terephthalic acid and its acid chloride (equivalent) are under $1.00/lb, p-phenylenediamine is in the $2.00/lb range, the meta, para hybrid diamines are probably in the $2.00 to $5.00/lb range, and far and away the most expensive of the monomers, by at least an order of magnitude, are the multifunctional monomers required for the heterocyclic PBX LCPs.

Future Cost Challenges

The cost challenges inherent in developing future thermotropic LCPs will be either (a) to develop higher-temperature properties utilizing the lower-cost hydroquinone or (b) to develop low-cost syntheses for the higher-temperature monomers or (c) to design and synthesize new low-cost aromatic monomers. An example of a very significant breakthrough via the second approach would be a direct coupling of phenol to produce 4,4'-biphenol in one step rather than via the existing processes, which either sulfonates the biphenyl followed by alkali fusion or couples 2,6-di-t-butylphenol at the 4 position, to form the 3,3',5,5'-tetra-t-butyl-4,4'-biphenol, and subsequent dealkylation. It should be noted that direct coupling of phenol has been achieved biologically but with no selectivity, all available carbon positions coupling at random. An example of the third approach would be a similar one-step coupling of benzoic acid to yield the 4,4'-bibenzoic acid.

As for the lyotropics, the biggest challenge is the development of lower-cost routes to the benzobisthiazole and benzobisoxazole polymers and by lower-cost routes to their multifunctional monomer precursors. Because of the very high price and therefore limited availability of these monomers, any advances in synthetic approaches would have a marked beneficial effect on their availability and on the future of the extremely high-performance materials

that can be made from them. Of considerable significance is the recent announcement by Dow that it is preparing a benzobisoxazole polymer in pilot-plant quantities.

UNDERSTANDING AND THEORY

Semiflexible LCPs

Liquid crystal formation by semiflexible polymers has been modeled by extensions of the Onsager method alluded to in Chapter 2. The relevant controlling parameter revealed by these theories (Doi and Edwards, 1986; Odijk, 1986) is the ratio of the persistence length to diameter of the polymer chain. Little experimental verification of these theories is yet in the literature. Dramatic predictions concerning the influence of macromolecular flexibility on the order parameter and concentration regime of biphasic stability are contained in these newer theories. These predictions should be tested with carefully obtained data on polymer systems that conform to the assumptions of the developments.

No totally general models exist yet for the anticipation of liquid crystallinity of semiflexible polymers at all concentrations. In particular, the thermotropic behavior is only poorly understood. The primary difficulty in developing a comprehensive picture of the thermodynamic aspects of LCPs lies in the fact that a high degree of coupling exists between all degrees of freedom in the system, internal and external to the polymer chains. Contrary to the situation in polymer melts and in amorphous systems, where chains can assume all conformations and the external constraints on a chain are essentially isotropic, in the liquid crystalline phase the necessity for the macromolecule to conform to the anisotropic spatial requirements of its environment reduces drastically its freedom in conformation (internal) and orientation (external). Chains in crystalline materials are similarly restricted, of course, but there the reduction of fully developed degrees of freedom for the chain is so drastic that in most cases only one conformation and one packing arrangement can exist; as a consequence, the analysis of crystalline systems has been mastered decades ago, and very simple rules can be applied (e.g., Natta's "equivalence principle," which states that in a polymer crystal the chain conformation must be a repeated sequence of local conformations). In liquid crystalline phases the molecules in a mesomorphic phase must adopt orientations, configurations, and a "packing" arrangement compatible with the weak, but not insignificant, constraints of symmetry and density of the mesophase. In consequence, both intra- and inter-molecular degrees of freedom, static and dynamic, are highly coupled, between molecules as well as within individual chains. This coupling is effective not only in thermotropic systems but also in lyotropic ones, as long as the concentration of polymer exceeds a critical value.

Polydispersity and Blends of Polymers

If systems with more than one component are involved in phase equilibria, one can, in general, expect an unequal distribution of the different species between the phases; LCPs are no exception. Three interesting situations exist: polymers not uniform with respect to molecular weight, mixtures of flexible and rigid chains, and LCP blends. To date, the first two situations have been addressed with some success:

- As prepared most LCPs are not uniform with respect to molecular weight and therefore are multicomponent systems; they may fractionate, especially in solution. The higher-average-molecular-weight species are found in the anisotropic phase; the lower-average-molecular-weight species accumulate in the isotropic phase. Computations have been performed for a variety of molecular weight distributions (see Flory, 1984, and citations therein).

- Mixtures of ideal random coils and rigid rods also fractionate strongly (Flory, 1984), even when the chains are composed of "identical" segments and are of identical molecular weight. The rigid species strongly prefer the anisotropic phase.

No theoretical treatment seems to have addressed the question of the blending of different mesogenic polymers. If both types of chains are constitutionally uniform, of equal rigidity and sufficiently long, the problem, to zeroth approximation, can be viewed in analogy to the blending of random coiling chains; in both cases the configurational entropy of mixing is very small and the enthalpy of mixing determines if blending is possible. One would therefore expect that LCPs mix only rarely. However, in flexible chains, miscibility can often be achieved by blending copolymers, and there is no reason why similar effects cannot be exploited in mesogenic polymers. The situation in LCPs is complicated, however, by the fact that the different species probably would be of different rigidity (exhibit different persistence lengths); one might speculate that for this reason blending would become even rarer than in flexible polymer mixtures, but only initial attempts at theoretically illuminating the situation has been put forward to date (DeMeusse and Jaffe, 1988).

Thermodynamic treatments of polymer-polymer mixing and of polymer mesophase formation have been treated by Flory (1986) and others (Flory and Ronca, 1979; Doi and Edwards, 1986; Odijk, 1986). The application of these concepts to LCP-containing blends is just beginning to appear in the literature. There is no reason to expect that these concepts will not provide an effective framework for understanding the phenomena observed in LCP-based polymer mixing. Comparison of LCP behavior in blending with that of low-molecular-weight LCs should also prove instructive. It is to be expected that miscibility between LCPs will be rare, as it is with conventional polymers. In contrast, most low-molecular-weight LCs of a given type are miscible with each other. The in-depth understanding of the physical chemistry of LCP blending will be an important cornerstone in defining the ultimate utility of LCP blends and should be rigorously pursued.

Dynamics

The dynamics of rigid rod systems have been investigated with intensity (Chandrasekhar, 1977; Doi and Edwards, 1986), and quantitative results are available for moderately concentrated solutions (below the transition to the nematic state). In the bulk, similar problems exist as for flexible chains. To date, only single polymer systems with chains of uniform molecular weight and flexibility (usually stiff rods) have been addressed. The following is known:

• The rotational constant in dilute (isotropic) solution of rod-like polymers grows with chain length approximately like $D_r \propto \ln(x)/x^3$. This is a very rapidly decreasing function of the aspect ratio x; long rigid rods rotate very slowly.

• In semidilute solutions (above the concentration where frequent intermolecular contacts occur, but still in the isotropic regime) of rigid-rod polymers, the rotational diffusion is attenuated by an additional dependence of the approximate form x^{-2} with respect to the one in dilute solution.

• In concentrated (i.e., anisotropic) solutions, and in the bulk phase, no rotational diffusion effectively exists.

• The translational diffusion coefficient parallel to the rod axis is roughly twice that perpendicular to that axis in dilute (isotropic) solution. Both diffusion constants grow as $D \propto \ln(x)/x$. This indicates a much less rapid decline than in the case of the rotational diffusivity.

• For semidilute (isotropic) solutions of rigid-rod polymers, the translational diffusion in the direction of the rod is roughly that for the same rod in dilute solution, but translation perpendicular to the rod is negligible.

• Very little is known about translational diffusion in the anisotropic solutions and in the bulk phase.

Many other dynamic phenomena have been addressed; of particular interest are the viscosity of solutions as a function of concentration (which follows the experimentally observed cusp curve) (Hermans, 1967) and the degree of order as a function of the concentration and external fields in anisotropic phases. Little quantitative information is available, however, in the latter cases.

Rheology

The anisotropic orientation in melt-processed molded parts cannot be predicted because a complete continuum theory for LCP rheology is not available. The classical theory of nematic liquid rheology developed by Leslie (1966, 1968) and Ericksen (1960, 1961) is inadequate for polymers because of the simplifying assumptions in the derivation: The stress is

assumed to be linear in the instantaneous rate of deformation, and the entropic free energy associated with local director gradients, which leads to an elastic "Frank" stress, is assumed to be quadratic. The theory does not take chain flexibility into account, and magnetic field experiments on thermotropic nematic melts (Moore and Denn, 1988) have indicated that there is creep in the Frank stress. The theory thus stands in relation to LCPs (particularly lyotropic solutions of very rigid molecules) in much the same way as the Newtonian fluid to conventional flexible polymers. Much can be gained by use of the Leslie-Ericksen theory, but results cannot be expected to be quantitative and may even be incorrect in qualitative terms for flows well outside the applicable range of the theory.

One important qualitative feature of LCP flow that does seem to be contained in the Leslie-Ericksen theory because of the presence of the entropic Frank elastic stress is the tendency of the director sometimes to adopt an orientation that is transverse to the plane of shear (Rey and Denn, 1989; Beris and Edwards, 1990). A continuum theory of LCPs by Doi (1981) is incomplete in that it does not contain any elastic contribution to the stress resulting from local director gradients; the Doi theory thus apparently cannot predict any phenomena associated with rapid spatial changes in orientation, although an extension of the theory that includes director gradient, has been reported (Beris and Edwards, 1990). Neither the Leslie-Ericksen nor the Doi theory has been applied to the flow of fluids with domain-like textures; it is unlikely that the Doi theory in its present form can be applied here because of the limitations already cited.

The rheological feature of LCPs that has been most exploited in applications other than fiber formation is the very high degree of shear thinning at all deformation rates (see Kulichikhin, 1989, and Muir and Porter, 1989, for recent reviews). It is this property that makes thermotropic melts attractive for molding applications with complex shapes and small passages. Qualitative models (Marrucci, 1984; Wissbrun, 1985) based on the relative motion of domains predict shear thinning at low deformation rates, but no adequate theory exists here either. It is possible that the presence of microcrystals in the melt is a factor in the shape of the flow curve, as well as long transients that are observed under conditions of apparent thermal stability.

The self-organizing feature of LCPs is an asset or a liability, depending on the shaping flow of interest. Predictive ability is lacking in any event, because the rheology is not understood in a fundamental way. Simulations of flow and orientation distributions in complex parts are unlikely to be correct in the absence of an adequate rheological theory, except in the case of a uniformly extensional flow of sufficient strength to effect uniaxial orientation (in which case no theory is needed). Progress in melt fabrication of molded parts that exploit the orientability of LCPs is unlikely until sufficient understanding of LCP behavior has been achieved to allow the modeling of geometrical and filling schemes that will lead to orientation distributions that approximate macroscopic isotropy and contain no rapid changes in orientation; the latter is particularly serious because of the poor self-adhesion of rigid polymers. It is not obvious that these problems can be overcome by conventional melt processing.

CONCLUSIONS

■   Rigid rod theories are in reasonably good order; macromolecular flexibility is manageable.

■   There are deficiencies in theories regarding blends of LCPs and LCPs with flexible polymers, and consequently there are no guidelines for experimental work in this area.

■   A lack of understanding of chain dynamics and rheology of LCPs is preventing solutions to processing problems such as the weld line, adhesion, and orientation development in molds.

RECOMMENDATIONS

■   Theoretical modeling leading to predictable distinctions between conventional isotropic phases and LC phases based on local primary and secondary chain structure is necessary to understand and develop new LCPs; intensified research should be encouraged.

■   More interactive research among theoreticians and experimentalists on aspects of blending LCPs is needed.

■   Theoretical studies of the fundamental dynamics and the rheology of LCPs should be encouraged, with accompanying experimentation on the relation between rheology and microstructure for the development and optimization of processing methods. The implications of available theories of LCP rheology should continue to be explored, but processing conclusions need to be examined with care because of the incompleteness of the existing theories.

PROCESSING

Lyotropic LCPs

Lyotropic LCPs have been the subject of intensive investigations. Molecular composites—a molecular dispersion of (lyotropic) rigid rod polymers in a (conventional) polymer matrix—have dominated the question of processing rigid rod LCPs. This novel state of matter remains elusive, however. The intricacies of retaining isolated rod-like molecules from dilute solution into the solid state are unknown, unpublished, proprietary, or a combination of these. Coagulants are critical to forming the molecular composite; their effect on both polymers needs to be addressed before fabricating and processing can be controlled.

Another problem lurking in the background concerns the retention of the level of molecular dispersion during use of such composites.

Aside from the intensive effort to fabricate molecular composites, there has been one more significant area of activity in processing lyotropic LCPs (apart from fiber production). This concerns attempts to fabricate biaxial structures—films—from PBX polymers. While there are reports of success at Foster-Miller using proprietary schemes, this work has been limited for the most part to bench-top scales (R. Lusignea, private communication). A major difficulty with evaluating the potential of this technology appears to be the severely limited availability of the PBX polymers. Pilot plant scale-up will be necessary before a meaningful assessment of film production is possible. However, it would appear that a viable interim solution could be explored—namely, investigating the feasibility of fabricating biaxial structures with commercially available lyotropic LCPs such as Kevlar® aramid. (See also the discussion of film formation in Chapter 2.)

Thermotropic LCPs

There are fundamental difficulties in traditional processing techniques (injection molding, extrusion, rotational molding, etc.). This may be generally attributed to intrinsic problems associated with highly ordered polymer melts. Self-adhesion in polymer melts, which is an important factor in the strength of parts that contain weld lines, is governed by diffusion of chains across interfaces. The rigid molecules of LCPs must diffuse a much greater distance to achieve adhesion than flexible polymers. It is for this reason that self-adhesion in LCPs is poor, both at weld lines and in regions of rapid orientation change. The "weld line" problem may be insurmountable at the molecular level for highly anisotropic melts and will require an engineering solution based on mold design. Herein we focus on novel processing possibilities for thermotropic LCPs.

Solid-State Forming

In studies of the extrusion of powder preforms of Xydar® (a terpolymer of p-hydroxybenzoic acid, terephthalic acid, and biphenol), workers at Alcoa found (Zaidi, 1988) that defect-free rods could be cold-extruded from the preforms only if the preform was annealed properly, the die was designed with the correct angle, and the temperature and rate of extrusion were held in the range that gives metal-like strain-hardening flow characteristics. This suggests that the constitutive behavior of solid LCPs as a function of temperature and pressure should be a critical area of research. It is also clear that the influence of pressure on solid-solid transitions would be an important conjunctive area of research between chemical structure and novel processing.

The explanation for cold-forming-induced optical clarity is still an issue. Contributions resulting from the small size of the crystalline domains in the formed material and the elimination of shrinkage voids have been mentioned. In the case of the LCPs, there is some indication that cold-formed shapes may be free of the skin-core effect and may enjoy outstanding machinability and wear characteristics relative to melt-formed material (Zaidi, 1988).

From a general point of view, solid-state forming does have its drawbacks. It often involves heavy, unconventional equipment and may require very expensive tooling. The parts may exhibit poorer dimensional stability than melt-formed ones, and extra allowance is often required for "spring-back" of the parts after removal from the dies. The severe orientation introduced by some forming processes may result in the tendency of the product to split—already a difficulty with LCPs. Because LCPs are relatively expensive polymers, the savings in energy and cycle time associated with solid-state forming may not have a significant effect on the overall cost of the part.

The use of powder preforms, which appears to be a way around the splitting problem, may hold little promise for exploitation of the ultimate strength properties of LCPs. If this proves to be the case, the entire combination—LCP fabricated with solid-state extrusion—becomes decidedly unattractive. Clearly, to accrue the full advantages of the preform extrusion technology, the constitutive behavior of solid LCPs as a function of temperature and pressure must be understood. In addition, the influence of pressure on solid-solid transitions would be an important conjunctive area of research for developing the connections between chemical structure and novel processing (Hsiao et al., 1988).

CONCLUSIONS

Lyotropics

An important objective of LCP processing technology is to develop strong materials for ultralight primary structures that are difficult to detect by radar and can withstand elevated temperatures. In the case of composites, the temperature resistance and tensile properties of fibers must also be combined with outstanding compressive properties and adhesion in fabrication schemes. For the LCP fibers to be effective in high-performance structural composites, they should also exhibit compressive strength that approaches the compressive properties of current carbon fibers.

Uniaxial structures prepared from liquid crystalline precursors (melts or solutions) exhibit outstanding tensile properties. For some time it was believed that the liquid crystalline state of the precursor during processing (spinning) was essential for achieving the molecular alignments and the perfection of structure that yield almost theoretical modulus and exceptional strengths—properties far above those of fibers produced from isotropic melts or solutions (Economy et al., 1970; Aharoni and Sibilia, 1978). Later, it was shown that the isotropic solutions of semirigid polymers produced at a low rate of elongational flow in the spin-way yield relatively weak fibers as spun. At high rates of deformation, however, the semirigid polymers yield properties close to those of aramids.

More recently, it was shown that even very flexible polymers, such as PE and PVA, can be converted into exceptionally strong fibers without becoming obviously liquid crystalline during the process of converting the isotropic solution into fiber. The quiescent liquid crystalline state is, therefore, beneficial for the preparation of strong fibers without after drawing but it

is not essential for all polymers. These observations must be borne in mind in assessing processing schemes and/or potential polymers for novel applications.

Thermotropics

Solid-state forming of LCPs is an immature area. It can be anticipated that many of the advantages of solid-state forming found with conventional semicrystalline polymers will accrue for LCPs. It is clear that there are unanticipated, unique properties that can be obtained by solid-state forming of powder preforms, but the basic science of this process as well as those using melt-formed preforms (e.g., sheets) needs to be investigated. The practical outcome of funding in this area would be an increase in the availability of high-performance LCP products for use in defense-related engineering projects. Not to be overlooked is the "knowledge" product: The exploration of solid-state forming techniques could lead to information concerning important phenomena such as the poor compressive strength of highly oriented LCPs.

RECOMMENDATIONS

■   Fabrication of biaxial film using readily available lyotropic LCPs should be investigated.

■   Other routes (nonmesomorphic gels) to high-modulus fibers should be explored.

■   Mold-design studies and experiments aimed at the weld line problem should be encouraged.

■   Solid-state forming of LCPs needs to be explored sufficiently to establish patterns allowing the performance of these novel processes to be compared with the extensive body of information already available for semicrystalline, random-coil polymers, as well as the definition of any advantages unique to LCPs.

■   For electro-optical applications, electric poling and associated fabrication processes need further study.

MECHANICAL PROPERTIES

Tensile Properties

Remote from major transitions, axial properties of solid-state filaments formed from LCPs are excellent and approach the theoretical limit in tensile modulus and exhibit extraordinary high tensile strength. Some typical properties of commercial fibers were shown in Figure 3.1. Transverse

properties, however, are poor, often 1 to 2 orders of magnitude lower than axial properties. This is inherent to highly anisotropic materials with a hierarchical morphology (Figure 2.13), and lateral weakness is expected to occur theoretically. These poor compressive properties (see, for example, Figure 4.1) limit the utility of LCPs in materials applications.
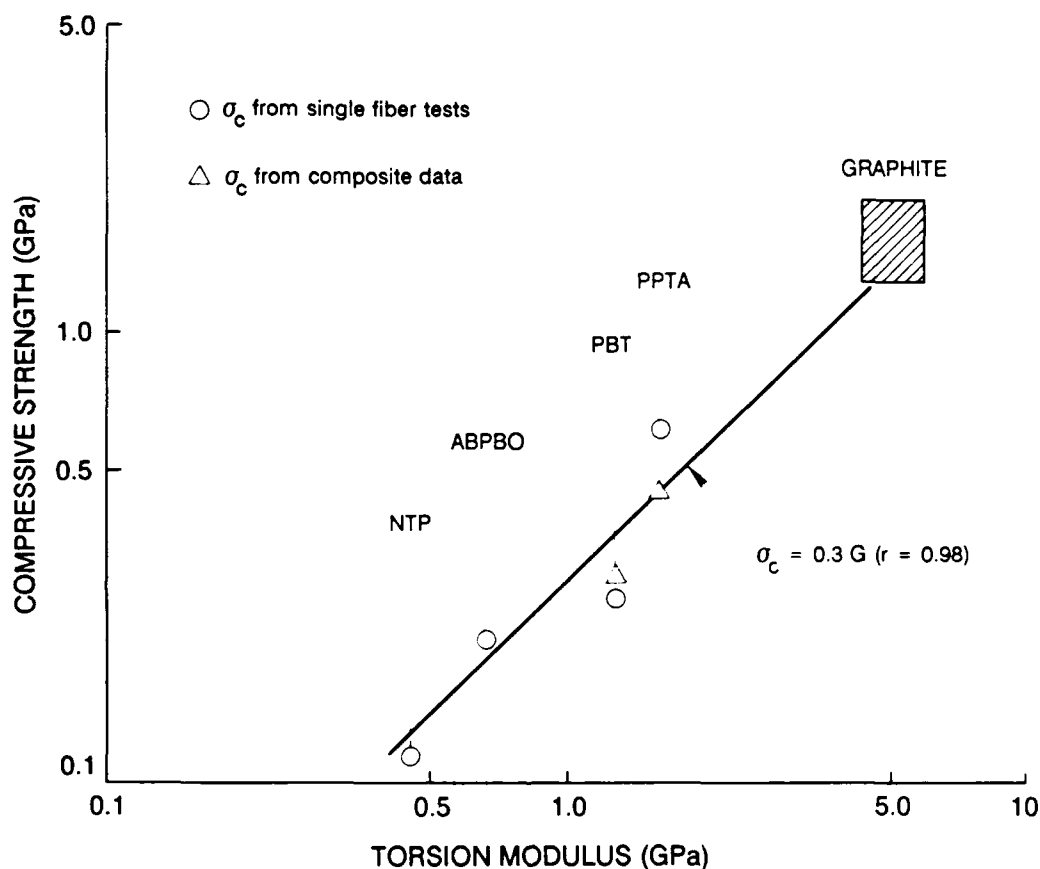
FIGURE 4.1 Compressive strength versus torsion modulus for some rigid rod polymers.

The outstanding problem is this: Can compressive properties of LCPs be improved without sacrificing desirable tensile properties? A major question in this regard is whether the fault is at the molecular or morphological level. Contemporary thinking suggests problems at a macroscopic level, i.e., interfibrillar bonding in the hierarchical fiber structures. This idea is reinforced because cross-linking (strengthening lateral intermolecular interactions) has not relieved the problem of poor compressive strength. Conversely, it has been argued by Jaffe and Yoon (1987) that essentially all of the mechanical properties of highly oriented LCPs can be explained on the basis of molecular parameters and that morphological features play only a minor role. This is probably not true in complex structures such as moldings and biaxial films. The issue remains to be resolved, however.

Cross-linking and blending of LCPs with random coil polymers (molecular composites) have been considered the most promising approaches to enhancing the transverse properties and compressive strength of LCP fibers. Cross-linking has been studied extensively with random coil fibers, such as nylons and poly(ethylene terephthalate), but the results fall short of expectations because the small improvements (if any) in compressive properties were offset by substantial losses in tensile properties. No successful composite technology based on cross-linked fibers and no successful cross-linking of LCP fibers has been reported as yet. A recent study (Grubb and Kearney, 1990) of the effect of formaldehyde cross-linking on properties of gel-drawn PVA offers a good overview of problems associated with this type of modification of uniaxial structures. A large and probably inevitable decrease in tensile modulus on cross-linking is particularly noteworthy. Unfortunately, the authors did not include the data on strength that usually show a much larger decrease on cross-linking than modulus.

In principle, the solution of the compressive strength problem through development of molecular composites appears to be very attractive. It must be noted, however, that authors invariably stress the improvements with LCP-random coil blends, but do not address the problem of compressive strength. Since a successful solution of this problem would be promptly revealed in technical or patent literature, it can be assumed that, heretofore, blending of LCPs and random coil polymers has failed to produce significant improvements in compressive strength. Consequently, we can speculate that poor adhesion between phases and the relatively coarse dispersions achieved so far have prevented successful development of a LCP-based system with a high compressive strength.

Thermal Behavior

The temperature fall-off of properties exhibited in Figure 4.2 is often characteristic of solids derived from thermotropic LCPs (see also Table 3.3). A substantial decrease in the tensile modulus is encountered between room temperature and temperatures characteristic of the α-transition in a particular LCP. This behavior may retard the utilization of LCP-based materials in cases where the LCP narrowly fulfills modulus criteria. Improvements in this area often lead to thermally intractable polymers, which in turn fail processing requirements.

Weld Line

Injection molding of three-dimensional items runs into the "weld line problem." Differently oriented director fields in LCPs do not adhere well to themselves. Moreover, when neighboring macromolecular axes are not parallel, interdiffusion is retarded. This fabrication problem, which is severe with thermotropic LCPs, requires clever mold design to ensure intimate mixing of director fields.
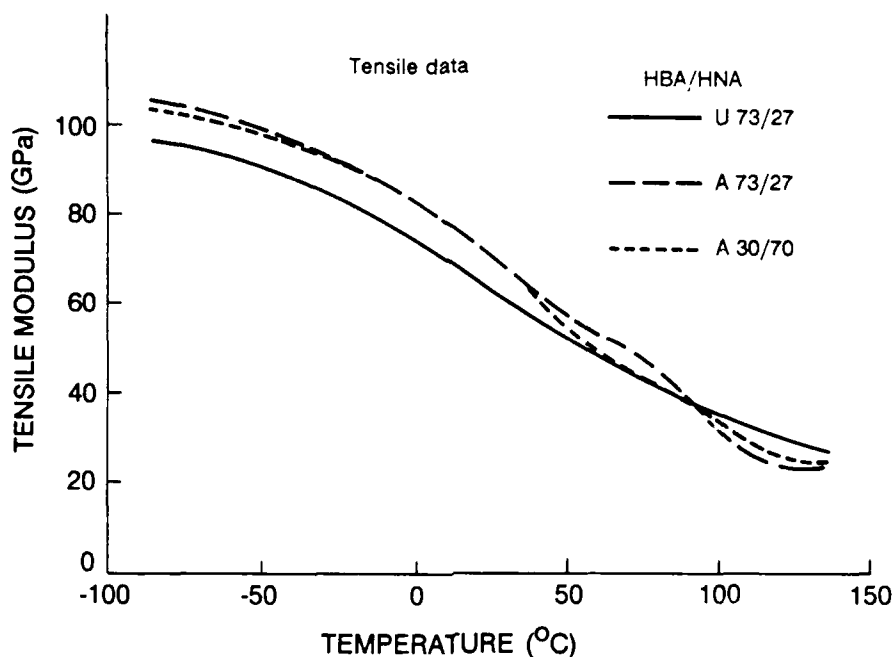
FIGURE 4.2 Temperature dependence of dynamic mechanical tensile data (10 Hz) for HBA-HNA copolymers (Davies and Wood, 1988).

CONCLUSIONS

■ Compressive failure currently limits widespread use of LCPs. Failure mechanisms and consequently potential solutions are not within reach.

■ Rapid deterioration of properties of LCPs with increasing temperature is another limitation that restricts use of these materials.

■ Conventional molding techniques exaggerate the weld line problem in LCPs.

RECOMMENDATIONS

■ A significant research effort should focus on the compressive failure problem.

■ Experimental and theoretical work on mold designs should be initiated.

■ Thermal properties of LCPs require molecular design solutions, and associated exploratory syntheses should be undertaken.

BLENDS AND COMPOSITES

Combining LCPs with other materials to improve overall property balance, exploit unique LCP performance, mitigate property deficiencies, and/or lower cost is an active and fruitful area of applied LCP research that may be divided into four subareas:

- Fillers for injection-molding resins
- Continuous-fiber-reinforced composites
- LCP-containing polymer blends
- Molecular composites

Fillers

The major application of the commercial thermotropic copolyesters is as a high-performance injection-molding resin. Fillers are employed in these systems to reduce overall part anisotropy, both in terms of flow direction to cross-flow property balance and control of skin-core effects. Fillers are also useful in minimizing part warpage and controlling the coefficient of thermal expansion. The fillers currently employed in LCP moldings are the same as those used with other thermoplastic engineering resins. Optimization has been limited to available materials, and little systematic research into optimizing filled LCPs can be found in the literature. Investigations into the effects of filler surface characteristics and geometry on molded part performance may prove a key to defining the limits to molded LCP part utility and should be encouraged.

Fiber-Reinforced Composites

The high-modulus, high-strength properties of LCP fibers have made them attractive candidates as reinforcing fibers for composites. Both thermotropic and lyotropic LCP fibers have been evaluated as reinforcing fibers, but published data for systems other than Kevlar® fiber are sparse. Typical data sets for LCP fibers may be found in Chapter 3. Tables 4.1A and 4.1B show properties of Kevlar® and PBZT relative to graphite fibers in epoxy composites.

The utility of LCP fibers in composites is limited by poor compressive properties and poor matrix adhesion. The physical structure responsible for low compressive strength does, however, provide advantages in damage tolerance and crash-worthiness. For example, para-aramid composites are metal-like in ductile energy absorption and respond to compressive stress noncatastrophically, unlike carbon composites, which have a brittle or catastrophic response (International Encyclopedia of Composites, 1989). The industry has recognized the benefits of combining the inherent damage tolerance of the LCP fibers with the compressive properties of carbon fiber in the form of hybrid composite structures.

TABLE 4.1A Properties of Unidirectional Epoxy* Composite with 60%
Fiber Loading, 0° Direction

Property	Kevlar®		Thornel® 300
	149 Aramid	49 Aramid	Graphite
Tensile Strength			
MPa	1450	1500	1420
Kpsi	210	218	206
Tensile Modulus			
GPa	107	79	133
Mpsi	15.6	11.5	19.3
% Conversion	99	99	97
Strain to Failure %	1.33	1.71	0.90
Compressive Strength			
MPa	193	234	—
Kpsi	28	34	—
Compressive Modulus			
GPa	73	66	—
Mpsi	10.6	9.5	—
Flexural Strength			
MPa	634	655	1192
Kpsi	92	95	173
Flexural Modulus			
GPa	79	67	116
Mpsi	11.5	9.7	16.8
Interlaminar Shear Strength			
MPa	57	59	70
Kpsi	8.3	8.6	10.2
Thermal Expansion Coefficient 10^{-6} m/m °C	+0.37	-2.33	—

*Epon® 828 epoxy cured with NMA/BDMA, laboratory impregnated.

Source:

• Riewald, P. G., A. K. Dhingra, and T. S. Chern. 1987. ICCM and ECCM, Sixth International and Second European Conference on Composite Materials, July 20-24, 1987. F. L. Matthews, N. C. R. Buskell, J. M. Hodgkinson, and J. Morton, eds. 5:5362-5370. New York: Elsevier Applied Science.

• Du Pont Company Publication. June 1987. Kevlar® 149, Properties and Characteristics of Yarn and Composites. E-95612.

TABLE 4.1B   Properties of Unidirectional Epoxy Composite with 60%
Fiber Loading*

Property	H.T. PBZT**	H.S. Graphite	Kevlar®49
Tensile			
Strength - MPa	1900	2100	1380
- Kpsi	270	300	200
Modulus - GPa	190	150	75.8
- Mpsi	28	21	11
Strain %	1.0	1.5	1.8
Poisson's Ratio	0.4	0.27	0.34
In-plane Shear			
Strength - MPa	35	69	—
- Kpsi	5	10	—
In-plane Shear			
Modulus - GPa	1.4	4.8	—
- Mpsi	0.2	0.7	—
Compressive			
Strength - MPa	200	1400	275
- Kpsi	30	200	40
Modulus - GPa	190	125	75.8
- Mpsi	27	18	11
Strain %	0.12	1.1	0.4
Flexural			
Strength - MPa	410	1600	—
- Kpsi	60	240	—
Modulus - GPa	140	120	—
- Mpsi	20	18	—
Short-Beam Shear			
- MPa	31	110	—
- Kpsi	4.5	16	—

*Hercules 3501-6 epoxy, laboratory impregnated.
**Heat treated PBZT.

Source:
• Uy, W. C. and J. F. Mammone. 1988. Canadian Textile J., pp. 54-63 (April).

• Wolfe, J. F. 1988. Polybenzothiazoles and Polybenzoxazoles. Pp. 601-635, in Encyclopedia of Polymer
Science and Engineering, Vol. 11, 2nd Ed. H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and
J. I. Kroschwitz, eds. New York: John Wiley and Sons.

The thermotropic copolyesters have been included in some recent studies evaluating thermoplastic resins for potential as thermoplastic matrices for continuous fiber reinforcement. Attractive features of the LCPs are low viscosity, good thermal stability, and high tensile properties. Negative features are poor adhesion to reinforcing fibers, property anisotropy, and poor compressive strength. Of these, the observation that the LCP matrix tends to orient along the direction of the reinforcing fibers has been most significant in dampening enthusiasm. One intriguing concept is the use of a LCP fiber to reinforce itself, almost as a macromolecular composite.

Further expansion of LCP fibers into composites is dependent on improving adhesion, a successful approach to the compressive strength problem, and demonstrated cost-effectiveness. Utility of the thermotropic LCPs as matrices is most dependent on the development of effective methods of orientation control.

LCP-Containing Polymer Blends

The motivation for considering LCP-containing blends is discussed in Chapter 2. As of 1988, the open literature dealing with LCP-containing polymer blends was sparse and difficult to search. Although it is beyond the scope of this report to examine and review in detail, the patent literature is probably the richest source of information. Useful reviews, however, are starting to appear (Browstow, 1988). Most of the LCP blend literature is highly observational in nature, and the data, because of the heavy impact of specific processing regimes and the use of difficult-to-obtain polymers, will be difficult to reproduce. Little attention has been given, for example, to separating the effects of polymer degradation or modification (transesterification, etc.) from the structures inherent in the blend. With the dearth of LCPs available worldwide, the number of LCPs blended with other polymers is necessarily small.

Blends of LCP and Conventional Polymers

Most of the work to date and the area with the greatest potential for commercial exploitation involves the blending of LCPs with conventional polymers. Although a few studies of solution blending with Kevlar® do exist (Tekayanagi et al., 1980), most of the work has centered on melt-blending thermotropic copolyesters (Vectra®, Xydar®) with engineering thermoplastics (PET, PEI, etc.). For convenience, this work may be separated into three blend regions based on LCP content, as shown in Table 4.2.

The potential utility of LCPs as a processing aid for high-viscosity conventional polymers was rigorously pursued by ICI in the early 1980s (Cogswell et al., 1983). Although the desired viscosity lowering appears to be dominated by the ratio of the viscosities of the components of the mixture, LCPs are unique in possessing both high molecular weight and low viscosity. Two modes of behavior have been observed: (a) blends with viscosity that

TABLE 4.2 LCP-Content Blending Regimes

Weight % LCP	General Description	Key References
0-15	Processing aid, viscosity reduction	Cogswell et al., 1983.
15-85	Self-reinforcing resins In situ composites	Kiss, 1987; Weiss et al., 1987.
85-100	Modified LCP	Patents

follows "rule of mixtures" based on the components, and (b) blends with viscosity lower than either component. This latter behavior is not understood. The use of LCPs as processing aids should be the easiest blend application to exploit commercially and, ultimately, may serve to render very difficult-to-process thermoplastics useful in common processes.

The most alluring blend regime to most researchers is the "in situ" composite where the LCP phase orients during processing to reinforce the plastic part. The effectiveness of this process is a function of the orientation imparted to the LCP in the chosen process. Published micrographs document morphologies ranging from spheres to fibrils. No quantification of morphology or correlations with process conditions have been published. Adhesion between the LCP and conventional polymer phases is clearly poor. During processing, stress transfer appears to be through the tortuosity of the phases, but this important factor has not been evaluated in depth. One consistent result in all studies is that the presence of an LCP phase renders the blend brittle (Kiss, 1987). This is probably a consequence of the poor interphase adhesion and requires clarification. Blending is unlikely to solve the weld line problem (Kiss, 1987). Mechanical properties of the blends, especially tensile modulus, follow expectations consistent with simple composite concepts in the absence of adhesion between matrix and reinforcement. For these blends to be useful commercially, the issues of adhesion and morphology control must be resolved. In addition, LCP in this application is in direct competition with glass and other reinforcing fibers, and hence the cost-effectiveness of the LCP approach must be established. Improved process equipment lifetime, reduced weight, and improved processibility are the likely LCP advantages. Unexamined in the literature is the degree to which nonstructural properties of LCP, i.e., very low gas permeability and high solvent resistance, carry over into blends.

It has been found that the presence of LCP may accelerate and presumably direct the crystallization of conventional polymers (Joseph et al., 1983). Blending biphasic polymers, such as the PET-polyHBA copolymers, may promote miscibility between the conventional phase of the biphasic polymer and another miscible conventional polymer, such as X7-G with poly(butylene terephthalate). These phenomena may offer direction in the search for useful compatibilizing agents for LCP-conventional polymer systems.

There are examples given in the literature (Froix, 1984) where the presence of small quantities of LCP blended with a conventional polymer results in mechanical properties significantly better than either component. No explanation for this observation has been advanced. The analogy of "introducing the lignin into a woody morphology consisting only of fibrin" is appealing but is not consistent with emerging models of LCP structure or LCP-conventional polymer interactions.

As sparse as the data set describing mainchain nematic LCP blends with conventional polymers is, it is rich compared to the almost nonexistent data on the blending of other types of LCPs—sidechain polymers, flexible spacer polymers, smectics, etc.

LCP-LCP Blends

Researchers have studied blends of thermotropic copolyesters with other thermotropic copolyesters, examining both blends of different copolymer ratios with identical chemistry (HBA-HNA type) and blends of different chemistries. Recognizing that each copolymer may be viewed as a blend (chain-to-chain variations, mer sequence variations), it was hypothesized that blending offered the means to "engineer the distribution." Initial results indicate that this is the case. Through such blending the behavior of both the mesophase and the solid state can be systematically modified. For example, transition temperatures can be shifted and power law indices of viscosity can be changed. These results also strongly imply that the "sequence matching" model of the thermotropic copolyesters in the solid state is more likely correct than the other models suggested in the literature (DeMeusse et al., 1988). Evidence was accumulated that LCP-LCP miscibility is not universal and that, at least in the mesophase, the basic concepts are consistent with the observed physical chemistry. The importance of this work is that it offers a direction for achieving sufficient insight into the nature of LCP structure-property relationships to design more appropriate molecules for given end uses. Related work indicates that transesterification may be responsible for some of these observations (J. Economy, private communication). Careful evaluation of the data cannot rule out transesterification effects, but it strongly suggests that transesterification is not causal in the observed behavior.

As in the case of LCP-conventional polymer blending, little information exists on the blending of LCPs of different inherent chain architecture or mesophase symmetry. Recent publications show phase separation in blends of sidechain nematics with other similar polymers or small-molecule analogues.

It is now established that, in contrast to the behavior of low-molecular-weight LCs, LCPs are often immiscible.

Investigations into the blending of LCPs with other polymers, conventional or LC, are in their infancy, and little is understood in detail. The literature is sparse, highly observational in nature, and very difficult to reproduce. Much of what is published is more an indication of what might be than an accurate data base from which to draw conclusions. It is clear, however, that, until the adhesion of LCP to other polymers and the rules controlling blend morphology are understood, the field will remain highly empirical and unlikely to yield many commercial successes. Conversely, for all the reasons that polymer blending is an attractive route to modified polymer products, blends containing LCPs are especially attractive. Systematic research to understand the physical chemistry of LCP-containing blends is likely to produce results of both commercial and scientific impact. This is true for LCP-conventional blends and all-LCP blend systems. Although initial work should focus on the commercial nematic polymers, other symmetries and phases should not be ignored. The area of compatibilizers ("molecular glue") is another concept worthy of support because of the high payback potential.

Molecular Composites

To date it is unclear whether a true molecular composite utilizing a molecularly dispersed LCP has been demonstrated, although materials possessing small agglomerations of rods (diameter of structure less than 50 Å) have been produced with very high tensile properties. It is not yet established, however, if these materials offer an advantage in tension. The concepts underlying molecular composite physics are consistent with the concepts of miscible blends; the materials being produced, even at the very small sizes of rod structures observed, fit the definitions associated with immiscible LCP-conventional polymer blends. Molecular composites can be treated with the already established framework of polymer-polymer mixing and do not require new concepts for accurate description. Success of molecular composites will be strongly linked to the economics of the processes and materials employed. Research in this area should be supported until a meaningful evaluation of cost-performance can be performed.

CONCLUSIONS

The combination of LCPs with other materials to control the balance of properties and improve cost-effectiveness is clearly an important technology area for increasing the overall utility of LCPs. The problems inhibiting the rapid development of this technology are the same as those slowing LCP acceptance in other areas, namely:

- High property anisotropy in finished parts,
- Poor compressive strength,
- Poor adhesion to conventional and mesogenic materials, and
- High cost.

This is not in contradiction to the observations that fillers and blending can mitigate many of these effects; rather, it is an important hint into what the underlying controlling parameters of the science must be.

RECOMMENDATIONS

From both the scientific and technological points of view, studies of the behavior of LCPs in multicomponent systems should be strongly supported. The following are specifically recommended:

■ Support research efforts to understand and exploit the combination of processing and fillers needed to provide a range of properties from fully isotropic to anisotropic.

■ Establish research efforts to understand and improve LCP adhesion to common composite matrices, fillers, and reinforcements, and other conventional and mesogenic polymers.

■ Establish systematic research efforts to understand and exploit the physical chemistry of LCP-containing polymer blends.

NONLINEAR OPTICAL PROPERTIES

In spite of the obvious advantages of organic NLO materials, there are major obstacles for utilizing polymers. In the case of second-order NLO applications, some obstacles are these:

• The uncertainty with respect to thermal stability of electric field-induced ordering in harsh environments, i.e., greater than 80°C.

• The small published data base on NLO properties, physical properties, and processing conditions for making active and passive structures in polymer films, and the sparse literature on second-order NLO properties of LCPs.

• The competitive advantage relative to $LiNbO_3$.

• The maturity of $LiNbO_3$-based technology.

• A lack of polymers designed specifically for SHG as well as device concepts and structures for utilizing them.

Although considerable recent progress has been made in achieving high nonlinear coefficients, additional work ranging from fundamental science to new materials development remains to be done if materials in this category are to reach their technological potential.

Liquid crystallinity has been shown to lead to enhanced alignment under certain poling conditions. The utilization of extremely high poling fields on amorphous systems, where a substantial fraction of dielectric saturation can be achieved, makes this less of a potential advantage. The anisotropic optical properties of LCPs would also have to be made extremely uniform to avoid scattering losses in bulk or waveguide devices.

The main benefit of liquid crystallinity may be one of imparting thermal stability to systems once they are poled. More esoteric applications might also exploit LCs. For example, the ferroelectric smectic C* phase, which is inherently noncentrosymmetric, might exhibit high degrees of macroscopic alignment and the desirable processing characteristics of a polymer. A polymeric system exhibiting this phase may require poling or other treatments to exhibit alignment, but the phase is inherently bistable as opposed to metastable in the case of poled thermoplastic. The smectic C* state combined with chromophore substituents designed for specific NLO applications would be an extremely attractive materials option.

For third-order NLO materials, the obstacles for utilization are more formidable:

• The state of understanding of third-order NLO properties based on the electronic structure of the constituent molecular or polymeric species is at a more rudimentary level, and a considerable diversity of opinion exists among scientists regarding the fundamental origin of nonlinear responses in these materials.

• Highly delocalized electronic structures are difficult to design into stable, easily processible polymeric structures.

• Approaches to increasing the nonresonant $\chi^{(3)}$ are unclear at this point.

• The stringent linear optical properties, including optical uniformity, transparency, and low scattering losses, combined with large $\chi^{(3)}$ required for device applications, have not yet been demonstrated, and formidable obstacles associated with -C-H vibrational overtones in the 1.3-μm and 1.55-μm regions remain to be addressed.

• Practical polymer processing conditions for achieving high degrees of orientation to enhance $\chi^{(3)}$ in formats suitable for waveguide formation have not yet been demonstrated.

Organic materials, because of their large nonresonant $\chi^{(3)}$ values, may constitute an enabling technology if progress can be made in the areas listed above. Low-dimensional electronic structures tend to exhibit the large values of $\chi^{(3)}$, since all of the oscillator strength is confined to one predominant direction in these materials. At the macroscopic level, uniaxial orientation of a material with low-dimensional molecular constituents or chains can increase $\chi^{(3)}$ by up to a factor of 5. Because of trade-off between n^2 and α, it will be important to achieve the factor of 5 by processing and fabrication

methods. Liquid crystallinity and other self-organizational influences and factors may offer routes to alignment, optical uniformity, and stability.

CONCLUSIONS

■ Inorganic crystals and thin films have advantages for some NLO applications, by virtue either of their function or the maturity of their technological position, but some may be displaced by organic polymeric thin-film materials because of cost and performance advantages; other applications may be made possible by the unique properties of organic and polymeric materials, assuming that fundamental advances can be made.

■ For second-order NLO processes, poled LCPs containing chromophores with a large molecular hyperpolarizability may offer advantages over amorphous polymers with respect to the degree and stability of the induced second-order nonlinear coefficient at the expense of more complex linear optical properties.

■ For third-order NLO processes, LCPs offer a route to achieving uniaxial alignment through processing and the associated potential for a five-fold increase in nonlinear coefficient relative to an electronically identical amorphous system, although considerable progress in fundamental understanding of microscopic processes, materials design and synthesis, and processing will be required to take advantage of this.

RECOMMENDATIONS

■ Research initiatives on organic and polymeric materials for second-order NLO addressing the issues of stability and magnitude of alignment by electric field poling, spontaneous or self-alignment, physical property studies, processing, and exploratory device utility should be supported. Priority should be given to interdisciplinary program where molecular and polymer design and synthesis, NLO studies, and polymer physical characterization can be combined.

■ Research initiatives aimed at improving the microscopic understanding of $\chi^{(3)}$ and testing models through structure property investigations should be supported. Because of the rudimentary state of theory, the data base of $\chi^{(3)}$ measurements on organic and polymeric structures should be expanded. Synthesis and characterization of new polymeric systems with an emphasis on increasing $\chi^{(3)}$ and achieving excellent linear optical properties including transparency at 0.85 μm, 1.3 μm, and 1.55 μm should be supported. Processing studies aimed at the unique requirements of waveguide nonlinear optics should be supported. Interdisciplinary studies of a fundamental nature as well as novel exploratory approaches should be encouraged.

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Appendix A

**FEDERAL FUNDING LEVELS AND SOURCES
FOR LCP RESEARCH**

Source	Amount in millions of dollars		
	FY88	FY89	FY90
Department of Defense			
Defense Advanced Research Projects Agency	0.316	0.908	0.300
Air Force Office of Scientific Research	1.8	1.8	1.8
Wright-Patterson Research and Development Center	4.4	4.40	4.40
Department of the Army - MTL	0.285	0.225	0.225
Department of the Army - ARO	0.326	0.510	0.590
Office of Naval Research	0.285	0.273	0.235
Department of Energy	0.6	0.65	0.75
National Aeronautics and Space Administration	0.025	0.05	0.10
National Science Foundation			
Polymers Program	0.6	0.6	0.7
MRL, MRG	1.1	1.1	1.1
Other	0.2	0.2	0.2
Totals	9.937	10.716	10.400

Appendix B

GLOSSARY OF ABBREVIATIONS

ABPBO	-	poly(2,5-benzoxazole)
AIBN	-	azobisisobutyronitrile
BP	-	biphenol
CW	-	chemical warfare
DMA	-	dynamic mechanical analysis
DS-2	-	a caustic mixture of chemicals used as a decontaminant
Ekonol®	-	Sumitomo polyester
FOM	-	figure of merit
gpd	-	grams per denier
Granlar®	-	Granmont/Montedison Polymer LCP
HBA	-	hydroxybenzoic acid
HNA	-	hydroxynaphthoic acid
HQ	-	hydroquinone
IA	-	isophthalic acid
ICI	-	Imperial Chemical Industries
IPN	-	interpenetrating network
Kevlar®	-	Du Pont lyotropic aramid LCP (Kevlar® aramid fiber) (See PPTA)
KTP	-	$KTiOPO_4$ (potassium titanyl phosphate)
LC(s)	-	liquid crystal(s)
LCP(s)	-	liquid crystalline polymer(s)
MQW	-	multiple quantum well
Nd:YAG	-	neodymium yttrium aluminum garnet
NLO	-	nonlinear optics or optical
NMR	-	nuclear magnetic resonance

NR	-	nonresonant
NTP	-	naphthalene containing thermotropic polyesters
PBO	-	polybenzobisoxazole
PBZT	-	polybenzobisthiazole
PBX	-	PBO and PBZT
PE	-	polyethylene
PEI	-	polyetherimide
PET	-	poly(ethylene terephthalate)
PPTA	-	Poly-p-phenyleneterephthalamide
PTS	-	poly(2,4-hexadiyn-1,6-diol-bis-p-toluene sulfonate)
PVA	-	poly(vinyl alcohol)
SEED	-	self-electro-optic device
SHG	-	second-harmonic generation
SRP(ICI)	-	ICI polyester LCP
TA	-	terephthalic acid
Vectra®	-	Hoechst-Celanese polyester LCP
Vectran HS®	-	Hoechst-Celanese LCP
Victrex®	-	ICI Engineering polymer
X7G®	-	Eastman polyester LCP
Xydar®	-	Amoco polyester LCP

Appendix C

BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS

EDWARD T. SAMULSKI received his B.S. degree from Clemson University and a Ph.D in chemistry from Princeton University. After postdoctoral research in Gröningen and Texas, he joined the faculty at the University of Connecticut. He is currently professor of chemistry at the University of North Carolina at Chapel Hill. His research interests are liquid crystals; biological macromolecules and synthetic polymers; and application of magnetic resonance techniques to study molecular dynamics of polymer solutions, melts and liquid crystal phases.

MORTON M. DENN received his B.S.E. degree from Princeton University and a Ph.D. in chemical engineering at the University of Minnesota. He was employed at the University of Delaware before joining the University of California at Berkeley, where he is professor of chemical engineering and Program Leader for Polymers and Composites in the Center for Advanced Materials at the Lawrence Berkeley Laboratory. He is a member of the National Academy of Engineering. His research interests are polymer processing; rheology; non-Newtonian fluid mechanics; polymer/nonpolymer surface interactions; and process simulation, stability, and control.

DONALD B. DUPRE received his B.A. degree from Rice University and M.A. and Ph.D. in chemistry at Princeton University. He was employed at North American Rockwell Corporation and is currently professor of chemistry at the University of Louisville. His research interests are laser light scattering spectroscopy and chemical physics of polymers and liquid crystals.

NATHAN D. FIELD received his B.S. degree from the City College of New York and Ph.D. in polymer chemistry from the Polytechnic Institute of Brooklyn. He is presently a consultant in Elkins Park, PA. Most recently he was vice-president of R&D at Dartco Manufacturing, Inc. where Xydar® LCP polyesters were developed. Prior to that, his experience included City University of New York, Playtex International, GAF Corporation, Atlantic Refining, and DuPont. His interests include liquid crystalline polymers, engineering resins, polymer blends, polymer structure-processing-property relationships, polymer synthesis, water soluble-swellable polymers, and surface-active chemistry.

ANSELM C. GRIFFIN III received his B.S. from the University of Mississippi and a Ph.D. in chemistry from the University of Texas at Austin. He is currently professor of chemistry and polymer science at the University of Southern Mississippi. His research interests are structure-property relationships in liquid crystals; solid state-chemistry; and liquid crystalline polymers.

MICHAEL JAFFE received his B.A. degree from Cornell University and a Ph.D. in chemistry from Rensselaer Polytechnic Institute. He is currently a research fellow at Hoechst-Celanese Research Division. His research interests are morphology of crystalline high polymers; transition behavior of polymers; and structure-property relationships of polymers and related materials.

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STEPHANIE L. KWOLEK received her B.S. degree at the Carnegie Institute of Technology and an honorary D.Sc. at Worcester Polytechnic Institute. Until retiring, she was research associate in the Textile Fibers Department, Pioneering Research Laboratory, E. I. DuPont de Nemours and Co., Inc. Her research interests are condensation polymers; high-temperature polymers; low-temperature interfacial and solution polymerizations; high-tenacity and high-modulus fibers and films; and liquid crystalline polymers and solutions.

MALCOLM B. POLK received his B.S. degree at the University of Illinois and a Ph.D. in chemistry at the University of Pennsylvania. He was employed by DuPont, Prairie View College, U.S. Department of the Interior, and Atlanta University. He is currently an associate professor at the School of Textile Engineering, Georgia Institute of Technology. His research interests are synthesis and characterization of liquid crystalline block copolyesters and copolyamides.

DUSAN C. PREVORSEK received B.S. and Ph.D. degrees in chemistry from the University of Ljubljana. He was employed by Goodyear Tire and Rubber Co. and the Textile Research Institute. He is currently manager of polymer science at Allied-Signal Corporation. His research interests are structure of complex organic molecules; theoretical and experimental viscoelasticity, diffusion, and fracture; textile and tire mechanics; synthesis and properties of ordered copolymers; polymer compatibility; interpenetrating networks; composites; and adhesion.

MONTGOMERY T. SHAW received B.ChE. and M.S. degrees from Cornell University and M.A. and Ph.D. degrees in chemistry from Princeton University. He was employed at Union Carbide Corporation. He is currently a professor at the University of Connecticut. His interests are research directed at relating the physical and chemical behavior of high polymers to the structure of the polymer and developing the theory and experiments to substantiate these relationships.

ULRICH SUTER received his diploma in chemical engineering and a Sc.D. at the Eidgenössische Technische Hochschule, Zurich. He was employed at that institution and at the Massachusetts Institute of Technology, and is currently a professor at the Eidgenössische Technische Hochschule. His research interests are physical polymer chemistry, statistical mechanics of polymers, amorphous polymers, and spectroscopy, including scattering and optical activity.

DAVID J. WILLIAMS received his B.S. degree from Le Moyne College and a Ph.D. in physical chemistry from the University of Rochester. He is currently manager of physical chemistry at Xerox Corporation. His research interests are mechanistics of photogeneration and transport of electronic charge in organic and polymeric materials; pulsed nuclear magnetic resonance; electron spin resonance; electrical measurements; and optical spectroscopy.